

ADA035702

(12)

FG

Report N00014-76-C-0340

GELATION OF OIL SLICKS BY AMINE CARBAMATES AS AN ADJUNCT TO
U. S. NAVY OIL SPILL RECOVERY OPERATIONS.

William W. Bannister ✓
Department of Chemistry
University of Lowell
Lowell, Massachusetts 01854

14 January 1977

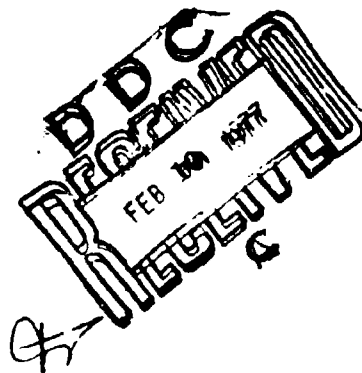
Final Report for Period: 15 October 1975 - 14 November 1976

"Approved for public release; distribution unlimited."

Prepared for:

OFFICE ON NAVAL RESEARCH
DEPARTMENT OF THE NAVY
800 North Quincy Street
Arlington, Virginia 22217

COPY AVAILABLE TO DDC DOES NOT
PERMIT FULLY LEGIBLE PRODUCTION



NAVAL 410050

COPY AVAILABLE TO DDC DOES NOT
PERMIT FULLY LEGIBLE PRODUCTION

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER (15) N00014-76-C-0348	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER (9)
4. TITLE (and Subtitle) GELATION OF OIL SLICKS BY AMINE CARBAMATES AS AN ADJUNCT TO U.S. NAVY OIL SPILL RECOVERY OPERATIONS.	5. TYPE OF REPORT & PERIOD COVERED FINAL REPORT 15 October 1975-14 Nov. 1976	
6. AUTHOR (10) William W. Bannister	7. PERFORMING ORG. REPORT NUMBER	
8. PERFORMING ORGANIZATION NAME AND ADDRESS University of Lowell Lowell, MA 01854	9. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0348 NEW	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research, Department of the Navy 800 North Quincy Street Arlington, VA 22217	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (12) 77p.	11. REPORT DATE 14 January 1977	
	12. NUMBER OF PAGES 76	
	13. SECURITY CLASS. (of this report) UNCLASSIFIED	
	14. DECLASSIFICATION/DOWNGRADING SCHEDULE	
15. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
16. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
17. SUPPLEMENTARY NOTES Copy available to DDC does not permit fully legible reproduction		
18. KEY WORDS (Continue on reverse side if necessary and identify by block number) Amine carbamates; Amine D; Amine D toxicity; amine gels; DIP Recovery Systems; Dynamic inclined plane recovery system; Fire hazard reduction; Fluorescers; Gelation; Oil recovery; Oil skimmers; Oil slick removal; Oil slicks.		
19. ABSTRACT (Continue on reverse side if necessary and identify by block number) Solutions of Amine D (dehydroabietylamine; 70%) in ethyl and benzyl alcohol, when sprayed on oil slicks to a concentration of about 10% and then treated with CO ₂ to form the carbamate, provides excellent gelation of the oil. Lab tests were performed on gel strengths, film thickness, temperature, and salinity for various fuels. A field test indicated that this system is very advantageous in recovery of oil slicks, in terms of ease of pick-up, immobilization of the oil, keeping the gelled oil from drifting back over cleared areas and greater viability of the gelled slick. (continued on reverse side)		

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 69 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

The toxicity of the Amine D is of a very low order, comparable to that of the oil slick itself; for water depths of over two feet, the toxicity is negligible. There is a significant (ca. 50%) reduction in evaporation rate of gelled, compared with ungelled hydrocarbons. This factor would be important in terms of reduced vapor hazards and perhaps fire hazards.

Ultraviolet fluorescers as additives to the gelling agent or to the oil slick itself were studied and found to have promise in terms of providing increased visibility for night time operations.

REC
U.S.
JUL 7 1964

DISTRIBUTION AVAILABLE TO CODES
ONLY SPECIAL

A

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

GELATION OF OIL SLICKS BY AMINE CARBAMATES AS AN ADJUNCT
TO U. S. NAVY OIL SPILL RECOVERY OPERATIONS

Acknowledgment

The following students at the University of Lowell provided valuable assistance on this project: Sheila L. Anderson, Paraschos Karahalios, David LeBlanc, William S. Bannister, John J. Cafarella, Jr., Steven Carr, Jeffrey A. Bannister, Ilidio Core-Real, Alan J. Gagnon, William G. Harris, Carolyn Murray, Peter J. Landers, Donald Malloy, David Landry, Philip P. Mykytiuk, Lorenzo C. Phillips, Christopher W. Ragland, Arthur L. Reed, Michael P. Santorsa, and David T. Zelonis. Other University of Lowell personnel included Dr. Howard W. Reynolds, Chairman of the Department of Chemical Engineering; John R. Pennace, staff assistant; and William W. Bannister of the Department of Chemistry (Principal Investigator).

Messrs. Ralph Bianchi (President of JBF Scientific Corporation) and Cesar Aguilar (also of JBF) headed up the research effort conducted at that company's facilities. Mr. William A. Curby, Head, Sias Biophysics Unit and Assistant Director of the Sias Research Laboratory, Lahey Clinic Foundation, was responsible for toxicology studies performed on this project. He was assisted by Robert Imbaro, Marta Kuzmiak, John Nugent, and Alan Slutsky.

It is with deep regret that we note the death of the Associate Investigator of this project, Dr. Howard W. Reynolds, on August 17, 1976. He was a valued friend and collaborator. This final report is dedicated to his memory.

TABLE OF CONTENTS

	Page
Acknowledgment	1
Table of Contents	2
List of figures	3
Objectives	4
Specific tasks	4
Results	6
Conclusions	31
Recommendations for futher work	32
Appendices:	
A. Acute toxicity of Hercules Amine D	33
B. Test plan for evaluation and demonstration of JBF Oil Skimmers in Boston Harbor	43
C. Technical Data, Amine D and Derivatives	61
D. Test operations at JBF Facilities, 20 September 1976	70
E. Correspondence from Scientific Officer, NRL	73

LIST OF FIGURES

	Page
Fig. 1. Laboratory tests of gelation.	12
2. Laboratory tests of gelation.	13
3. Application of amine from 3.5 gallon spray can.	17
4. Carbonation, using powdered Dry Ice.	18
5. Gelled oil after amine spraying and carbonation.	19
6. Another view of the gelled oil.	20
7. Gelled oil and ungelled oil with Navy Piston Film.	21
8. DIP craft with ungelled oil.	23
9. DIP craft with gelled oil.	24
10. Forward view of DIP craft in process of recovering gelled oil.	25
11. Volatility measuring device.	27
12. Flame tests.	30
13. Normal blood cells.	39
14. Red blood cells of fish exposed to fuel oil.	39
15. Nuclei appear to project from cells, and shedding of cytoplasm is evident.	40
16. Isolated nuclei of red blood cells.	40
17. Cytoplasmic membranes from oil/Amine D experiments.	41
18. Red blood cells of fish exposed to Amine D.	41
19. Cytoplasmic membranes as projections begin to develop.	42
20. Vacuoles appear, possibly taken in by pseudopodic action.	42

FINAL REPORT: "GELATION OF OIL SPILLS BY AMINE CARBAMATES AS AN ADJUNCT
TO U.S. NAVY OIL SPILL RECOVERY OPERATIONS"

Contract No. N00014-76-C-0349

Office of Naval Research
Department of the Navy

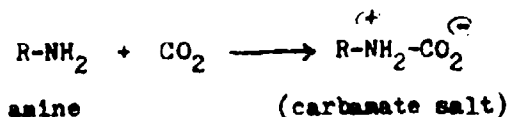
Contract Period: 15 October 1975 - 14 November 1976

OBJECTIVES

The objectives of this research project, as stated in the original proposal submitted 27 May 1975, were to investigate the feasibility of using commercially available aliphatic amines in the form of carbamate salts as gelling agents for oil slicks at sea or on inland waters to:

1. Restrain the spreading of oil slicks.
2. Improve the visibility of the boundaries of oil slicks undergoing retrieval operations.
3. Facilitate and enhance the yield of harvesting of oil slicks, using existing U.S. Navy oil spill removal equipment.

(The process embodied in the proposal and project is the reaction between high molecular weight aliphatic amines in hydrocarbon or other solvent to produce gels upon treatment with carbon dioxide, to produce carbamate salts:



(With a sufficiently high molecular weight amine ($R = C_{12}$ or higher) the resulting carbamate salt has sufficient hydrophobic character to permit gelation of the solvent, even in the presence of water.)

The specific tasks embodied in the original proposal, as amended by the specifications in the awarding contract, included the following:

- A. Investigation of the rheology of gelled oil slicks.

Included in the rheology studies were the following considerations:

1. Structure/property correlations.
2. Temperature and concentration effects.
3. Optimization of gelling systems.
4. Investigation of use with Navy Piston Film.

The awarding contract specifications further stipulated:

Laboratory gelling studies should be applied to petroleum products likely to be involved in Navy spills; especially NSFO, Navy Distillate and JP-5. A gelling agent should be selected which is most effective on these fuel types.

Rheological measurements should be on pure compounds.

The influence of spill thickness on gelation effectiveness should be investigated.

The interplay between gelation techniques and other multi-element confinement methods (water streams, piston film, etc.) should be investigated.

B. Investigation of toxicity of alternative agents.

(It was established that test tanks of sea water were to be set up with established colonies of a fish species such as Fundulus heteroclitus. On the surface of these tanks oil slicks were to be gelled and subsequently removed. Blood streams of the fish were to be sampled and compared with control populations.

C. Development of a test plan and receipt of government approval.

Depending on favorable results in Tasks A. and B., a test plan for a field test in Boston Harbor was to be developed and submitted to the EPA, Coast Guard, state and municipal water control authorities.

D. Investigation of practical methods of application of gelling systems to oil slicks.

This task was to include a determination of optimum method of delivery of the amine to an oil slick, evaluating nozzle, pump and similar systems, and optimum means of delivery of carbon dioxide.

E. Building the test system.

F. Testing the system in Boston Harbor.

(Tasks E. and F. depended on the outcome of Tasks D. and C., respectively.)

G., H. (These tasks referred to the submission of reports.)

Several additional tasks and objectives developed as spin-off ramifications during the course of the project. These included the following:

I. Reduction of volatility by gellation of hydrocarbons.

J. Reduction of flammability by gelation of hydrocarbons.

K. Ultra-violet fluorescence as a means of enhancing visibility of gelled and ungelled oil slicks.

RESULTS.

A. Rheology of gelled oil slicks.

Our initial efforts were directed toward determination of an optimum cold weather gelling agent which would provide sufficient gelling properties to most oil systems down to 20° F, remaining fluid enough to apply as a spray onto oil slicks at such temperatures. Initially we concentrated on mixtures of commercially available straight chain amines; a satisfactory agent system for AVCAS 145 (less so for JP-5, Navy Residual Special Fuel Oil #6, and similar oils) was found to be a mixture of 40 g. dodecylamine, 25 g. tetradecylamine, and 4.5 g. hexadecylamine in solution with 100 g. methyl alcohol. By far the best system, however, was a mixture of 70% dehydroabietylamine ("Amine D", as manufactured by Hercules Corp.) and either 30% ethyl alcohol or 15% ethyl alcohol and 15% benzyl alcohol. For practical considerations the latter formulation (with benzyl alcohol) was found to be superior for most situations. Apparently, the alcohol functions not only to lower the viscosity (Amine D is a highly viscous fluid over all operational temperatures; see Appendix C for a discussion of the

properties of Amine D), but also to provide sufficient polarity within the hydrocarbon solution of the carbamate for the ionic $\text{H-NH}_2\text{-CO}_2^-$ carbamate gelant to set up in a crystal lattice with water, which is also taken up into the gel. In a number of different tests it was observed that gelation commences at the water-oil interface, and that the gel grows upward from this boundary throughout the oil. As much as half the gel, depending on the nature of the hydrocarbon solvent, may be water; thus, on carbonation of a solution of 90% dodecane and 10% of a solution of 70% Amine D, 15% ethyl alcohol and 15% benzyl alcohol in a 3 mm thick film on water, a 6.1 mm thick gel occurred. This tendency for a floating oil slick to be doubled in thickness by admixture with amine and subsequent carbonation could be of distinct advantage in terms of harvesting very thin oil slicks.

Film thickness does not seem to be a significant factor in extent or rate of gelation. Various oils in thicknesses of 0.5 mm, 1 mm, 2 mm, 3 mm, 5 mm, and 6 mm all underwent gelation at approximately the same rate for a given oil and with 10% amine/alcohol additive; with JP-5 as the oil, gelation took place in less than 8 minutes, at all thicknesses. Even sheen appears to be gelled -- although it is still iridescent, gelled sheen is very easily moved around and picked up; it does not approach a solid state, however, as do reasonably thick (i.e., 0.5 mm or greater) layers.

Water temperature is rather important for some hydrocarbons. Thus, No. 2 Fuel Oil does not gel easily, and gel strength is materially reduced at temperatures above 70° F. AVGAS 145 appears to be more easily gelled at temperatures up to 80° F. (Below 70° No. 2 Fuel Oil gels very readily.)

In an attempt to obtain quantitative measurements of gel strengths for various combinations of different hydrocarbons and different amine gelants, we initially intended to measure comparative gel strengths by comparing rates of creep or spread of the gelled oil slick. However, all gels were so rigid that no creep could be observed in any instance. We were able to construct a Bloom-type gelometer, using specifications provided by the Atlantic Gelatin Co. of Woburn, Massachusetts. Measurements were not reproducible, however, using this apparatus.

A very promising device which we contrived for this purpose consists very simply of a vertical meter stick, at the base of which is placed the gel to be tested, and at a height of which of 25 cm. is placed a spherical steel ball of 12 mm diameter. Upon dropping the ball into the gel, various depths of

penetration are achieved, depending on the strength of the gel, which depths will serve as an index of the gel strength. Unfortunately, time did not permit the investigation of a meaningful enough number of different types of gels to provide a basis for quantitative measurements.

We were able to make qualitative observations which enable us to indicate desirable and undesirable features inherent in gelling agents and in the hydrocarbon solvents.

In investigating the amine gelants, oil slicks on water surfaces were not utilized, since some of the amine carbamates were so soluble in water these would not have remained in the hydrocarbon, but rather would be dissolved into the water. Dodecane was used as the hydrocarbon in these studies, with a 10% solution of the amine-ethyl alcohol-benzyl alcohol (70%-15%-15% by volume) mixture and an additional 10% of the total volume of hydrocarbon solution as water added to facilitate gelation. Relative to unsubstituted aliphatic amines, aromatic substituents located one or more carbons away from the amino group provided increased gel strength. Alicyclic substituents (as in cyclohexylamine) are also conducive to gel strength. Polycyclic structure (as is the case in Amine D and with 1-aminomethylnaphthalene) in the gelant is very conducive to gelation and gel strength. Olefinic character (e.g., oleylamine) is weakening, as is branching near the amino group. Primary amines are stronger than secondary amines as gelling agents, and tertiary amines are extremely poor.

Pure hydrocarbons give greatest gel strengths, with multi-component mixtures such as is the case with No. 2 Fuel Oil, JP-5, Navy Residual Fuel Oil #6, etc. are less effective. Unsaturation in the hydrocarbon is an especially desirable feature; aromatic and olefinic hydrocarbons are superior to saturated hydrocarbons. Chain branching and alicyclic character are weakening. Higher chain lengths are favored over lower chain lengths. The stronger gels were formed more quickly than the weaker gels; benzene gels almost immediately, whereas JP-5 required 6 minutes. (In each case, in this investigation, a 12% solution of a mixture of 70% Amine D, 15% ethyl alcohol, and 15% benzyl alcohol was prepared with the hydrocarbon, this floating as a 10 mm thick slick over water.) The hydrocarbons investigated were ranked qualitatively in order of decreasing gel strength as per the following order:

Benzene
1-Dodecene
Dodecane
Hexane
Cyclohexane
2,2,4-Trimethylpentane
AVGAS 145
No. 2 Fuel Oil
JP-5
Navy Residual Special Fuel Oil #6

(Except for Navy Residual Special Fuel Oil #6, all the hydrocarbons listed above gave satisfactory gel strengths in terms of indicated ability to be harvested in typical harbor or ocean conditions, i.e., much more readily than the ungelled hydrocarbon. Navy Residual Special Fuel Oil #6 was gelled to some extent, but it was sufficiently highly viscous to begin with, so that it would presumably be difficult to impart to it any significant increase in tenacity. Because of its very high viscosity, it was extremely difficult to produce a homogeneous solution of the amine gelant with this oil; under any conceivable harbor or ocean situation this would not be at all practical.)

The interplay between gelation techniques and other multi-element confinement methods was investigated. On a laboratory scale, it was found, as we expected, that the clumps of gelled oil could be moved around very easily using either air or water jets, and by the same techniques directed into any position. On both laboratory and field test scales (for the latter, see section H. of this report), the alcoholic solutions of Amine D were found totally compatible with Navy Piston Oil Film: gel formation occurred without apparent inhibition when Piston Oil Film was mixed with the amine prior to spraying over oil slick surfaces; and "loose" (ungelled) oil mixed with gelled oil was successfully herded by application of minute amounts of Piston Oil Film.

H. Investigation of toxicity of Amine D to marine organisms.

This study was performed in toto by workers at Sias Research Laboratories.

Initially, the toxicity studies were begun using the mixture of dodecyl, tetradecyl, and hexadecylamines cited in section A. of this report. This agent was abandoned, however, when we ascertained early in the overall investigation that Amine D solutions would be the most promising agents of those studied up

to that time, and all marine organism toxicology studies were performed using Amine D with enough ethyl alcohol to provide sufficiently low viscosity. (The superior performance provided by admixture of benzyl alcohol to the Amine D - ethyl alcohol mixture was not ascertained until well after the Amine D toxicology studies had commenced. Therefore, it was not considered feasible to recommence the studies using the benzyl alcohol additive; moreover, the slight toxicity that might be imparted by the benzyl alcohol to the mixture, by itself, was felt to be detrimental to the interpretation of extent of toxicity of the Amine D.)

The final report provided by the Sloan Research Laboratory unit is included in this Report, as Appendix B. By way of brief summary of the toxicology studies, the following facts were ascertained:

1. Amine D by itself is of about the same or perhaps slightly greater toxicity than No. 2 Fuel Oil alone, with synergistically greater (though not much so) toxicity of mixtures of Amine D and No. 2 Fuel Oil relative to the toxicity of the oil alone.
2. The dilution effects provided in any conceivable operational situation, i.e., in water depths of more than two feet, would completely eliminate any toxicity effect, exerted by the amine. (The amine is extremely insoluble in water.)
3. Even in the case of very shallow water operations (i.e., with a water column of less than two feet), toxic effects could be acceptably reduced if clean-up operations were to ensue in a reasonably short time interval (i.e., within an hour or two) after application of the amine to a floating oil slick.
4. Essentially no greater toxicity hazard is posed by the use of Amine D than is posed by the existence of the oil slick itself.

C. Development of a test plan and receipt of government approval.

A Master Test Plan (see Appendix B) was prepared by the JBF Scientific Corporation for a field test in Boston Harbor. As originally prepared, no provision was included for use of the amine gelling agent; this was to be provided by amendment, pending the availability of favorable toxicology data.

The changeover from toxicology studies on the dodecyl-/tetradecyl-/hexadecylamine system to the Amine D system posed one element of delay, however. Moreover, the relatively low toxicity indicated by the manufacturers of Amine D led us to assume initially that there would be insignificant marine organism toxicity apparent at the onset of the studies. The extra effort and time required to demonstrate conclusively that the operational hazards would indeed be insignificant made it clear by summer that the incorporation of toxicology data sufficient to ensure government approval of use of the Amine D agent would be infeasible, at least in time to ensure an autumn test in Boston Harbor.

Accordingly, we requested and received permission to perform the field test in the JBF test tank at the new JBF Corporation facilities in Wilmington, Massachusetts.

D. Investigation of practical methods of application of gelling systems to oil slicks.

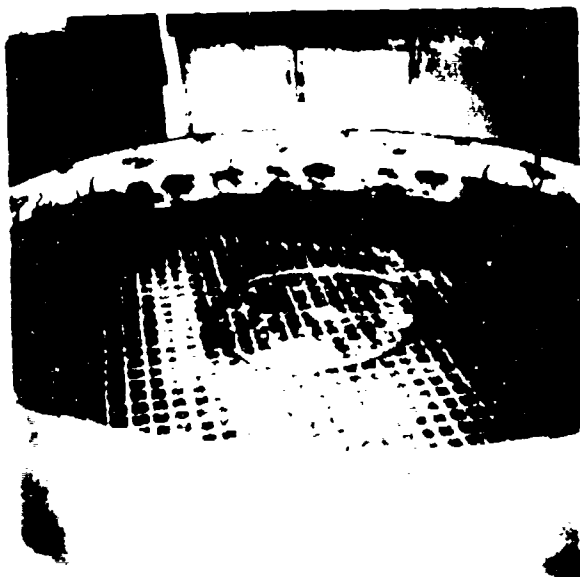
For laboratory scale studies of methods of application of the gelant to oil slicks, an eight-foot diameter plastic swimming pool was set up. A 40 cm. boom was floated in the pool, inside of which hoop was placed the oil to be gelled. (See Figure 1, page 12.)

Our first effort involved the use of a simple garden sprinkling can, from which we applied as uniformly as possible the requisite amount of Amine D solution to the oil to afford (usually) a 10% solution of the Amine D mixture with ethyl and benzyl alcohols (70% Amine D, 15% each for the alcohols) in the oil. (Thus, a 7% amine solution would be afforded.) The success in attaining a good uniform gel by this technique is shown in Figure 2 (page 13).

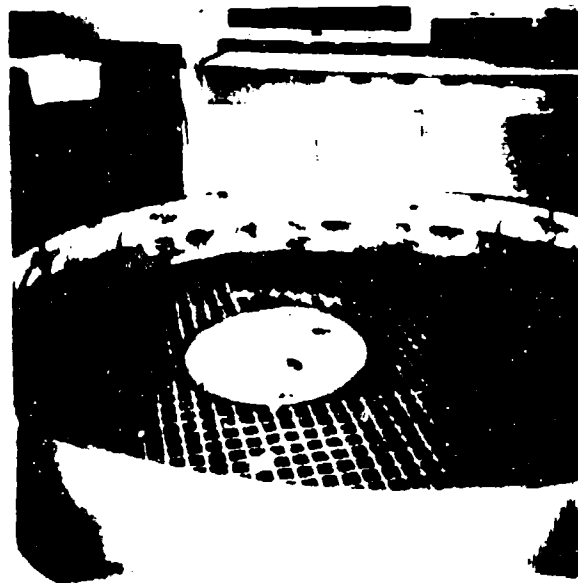
Encouraged by these results, we then turned to a paint spray gun as a prototype spraying device for applying the amine. In the reservoir of the sprayer was placed the requisite volume of Amine D solution. CO₂ gas was then released through the spraying apparatus, in either of two modes:

- (a) As a propelling gas, forcing the amine contents through the spraying nozzle by being led into the reservoir itself. This was the most efficient method, in terms of pressure required and spray droplet size. However, the carbamation of the amine in the reservoir proceeded quickly and thoroughly enough that within a few seconds

Figure 1.



A. A solution of 35 ml. Amine D, 15 ml. benzyl alcohol, and 340 ml. No. 2 fuel oil (total volume, 378 ml; 7% Amine D) placed within 40 cm. diameter hoop. 30 g. powdered Dry Ice was then applied.



B. Six minutes later; gellation is complete.



C. Gel strength is sufficient to permit removal of hoop; gelled oil does not spread.

Figure 2.



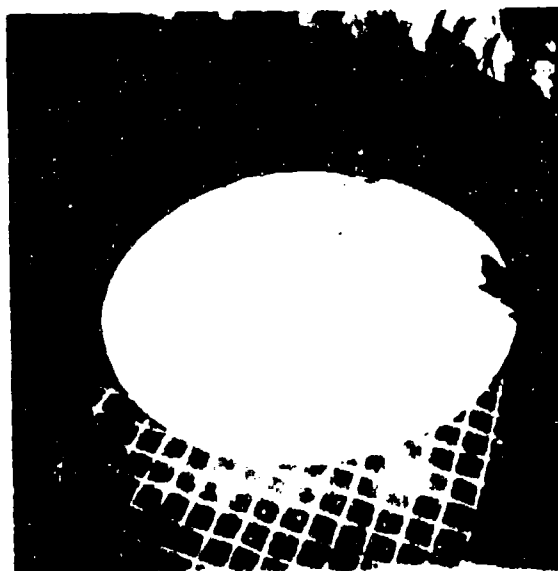
A. 340 ml. No. 2 Fuel Oil is being sprinkled with solution of 35 ml. Amine D, 17.5 ml. benzyl alcohol, and 17.5 ml. ethyl alcohol.



B. Hooped area (40 cm. diameter), 2 minutes after treatment with 30 g. powdered Dry Ice. Gel is beginning to form.



C. Six minutes after amine treatment, gel is essentially completely formed.



D. Gel strength is sufficient to permit removal of hoop; gelled oil does not spread.

the nozzle orifices became plugged up by the semi-solid amine carbamate (formed by the reaction of the amine with the propellant CO_2 gas).

- (b) with the CO_2 gas bypassing the reservoir, drawing up the amine solution by suction (the Venturi principle). In this mode, the amount of pressure required (in excess of 50 psi) to effect pickup of the amine solution caused the formation of a fog of very fine liquid droplets in the spray. This was an adverse effect for two reasons:

- (1) Even very slight wind velocities in the spraying area were sufficient to blow the spray off the desired spray pattern; it was determined that less than one fourth of the desired quantity of amine intended to be delivered to a given oil slick area actually landed on that area, even under ideal conditions. Larger liquid drop sizes were required.
- (2) Most importantly, the amine solution in this fog form posed a severe choking problem. It is conceivable that, despite the low toxicity of Amine D, a very serious health problem could result from use of Amine D fogs. One possible explanation of the choking character of the fog could be formation of Amine D carbamate upon respiration of the fog into the lungs, by reaction of the amine with CO_2 in the lung, and clogging of the alveoli in the lung by the gummy particles of the carbamate. For this reason, it is recommended that amine solutions NOT be applied as fogs.

Another device with which we experimented was a 35 lb. fire extinguisher of the CO_2 type, in the horn of which was inserted a Devilbiss atomizer (of the kind used for throat spraying). Pressurized nitrogen (25 psi) was used to spray the amine solution through the atomizer into the horn of the extinguisher, which was simultaneously activated, releasing solid and gaseous CO_2 intermixed with the amine spray. Excellent results were obtained for up to a half minute of spraying, indicating that the Amine D could be sprayed onto the oil slick as the pre-formed carbamate and still produce gelation of the hydrocarbon oil

slick. However, the cold frozen CO_2 in each instance caused eventual freeze-up in the atomizer of the Amine D solution. Moreover, the amount of CO_2 required for this type of operation was astronomically large; a typical experiment would utilize 35 pounds of CO_2 in the extinguisher to mix with $\frac{1}{2}$ lb. of amine D solution.

The fact that the carbamate could be preformed and then applied to the oil slick and still obtain gelation encouraged us to experiment with Amine D carbamate (which is a gummy white solid) by itself and in various solutions. We were uniformly unsuccessful in this, although we are still working on this possibility, since it would obviate the requirement for carrying CO_2 in any form on the recovery craft. With the Amine D carbamate itself, the gummy character of the solid prevented any reduction to fine particle form, which in turn would be necessary in order to achieve good homogeneous distribution in an oil slick. The amine carbamate is reasonably soluble in such protic solvents as methyl and ethyl alcohols, and also in DMSO. However, these solvents tend to carry the amine solute into the water rather than into the oil slick. Although the carbamate then re-precipitates (on contact with the water), the solid carbamate in the water has little if any tendency to mix with the overlying oil.

Our earlier success with the gravity fed garden sprinkler thus brought us back to this type of system, with the one modification of providing a means of pressurizing the amine solution so that a greater area of application could be realized. After attempting to construct some laboratory prototypes, all of which proved unwieldy, a 3.3 gallon Chapin No. 135 hand pumped compressed air garden sprayer was selected as being acceptable for use in field test operations. Figure 3 (page 17) illustrates the use of this sprayer.

E. Building the test system.

(See discussion immediately above.)

F. Testing the system in the JBF test tank (vice Boston Harbor).

As indicated in the discussion under C. above, it had proved infeasible to arrange a test of the system in Boston Harbor, as had been provided in the original proposal, and accordingly we had requested and received permission to

perform the field test in the JBF test tank at Wilmington, Massachusetts. For this test, scheduled for 20-21 September 1976, we were requested by the NRL Scientific Officer to achieve the following goals (correspondence of 27 July 1976): (see Appendix E)

- (1) Determination of the feasibility of in situ oil spill gelation using the developed amine carbamate approach under field conditions.
- (2) Evaluation of the effectiveness of devices for applying gelation agents.
- (3) Studies of the ability of oil-spill removal systems to harvest the gelled petroleum oil.
- (4) Determination of the possibility of premixing the amine and CO₂ prior to their contact with the floating oil and the properties of the gel produced by such a procedure.
- (5) Oil-collecting agents (Piston Film) will be used to confine some of the test spills to determine the advantage of preventing spreading of the spill prior to gelation.

For the test operation, the test tank was boomed off into two small and two large quadrants. The sequence of events for each of the quadrants utilized in the test operation is provided in this report as Appendix D. (Note: the optional nighttime fluorescence test was not performed.) A discussion of each of the phases of the test operation follows.

I. Small quadrant test: (see Figures 3, 4, 5, 6, & 7, pp. 17 - 21)

A. Sequence:

1. Apply 2 gallons of Diesel fuel to surface of pool.
2. Apply small quantity of Piston Oil Film to assist in containment of slick.
3. Spray 0.3 gal. (making for 15% vol./vol. concentration) of solution of Amine D (70% D, 15% ethyl alcohol, 15% benzyl alcohol) on surface of slick.
4. Apply powdered Dry Ice. Let stand for 5 minutes for gelation.
5. Recover gelled slick using sieve.
6. Apply Piston Film to any residual ungelled oil.

[illegible]

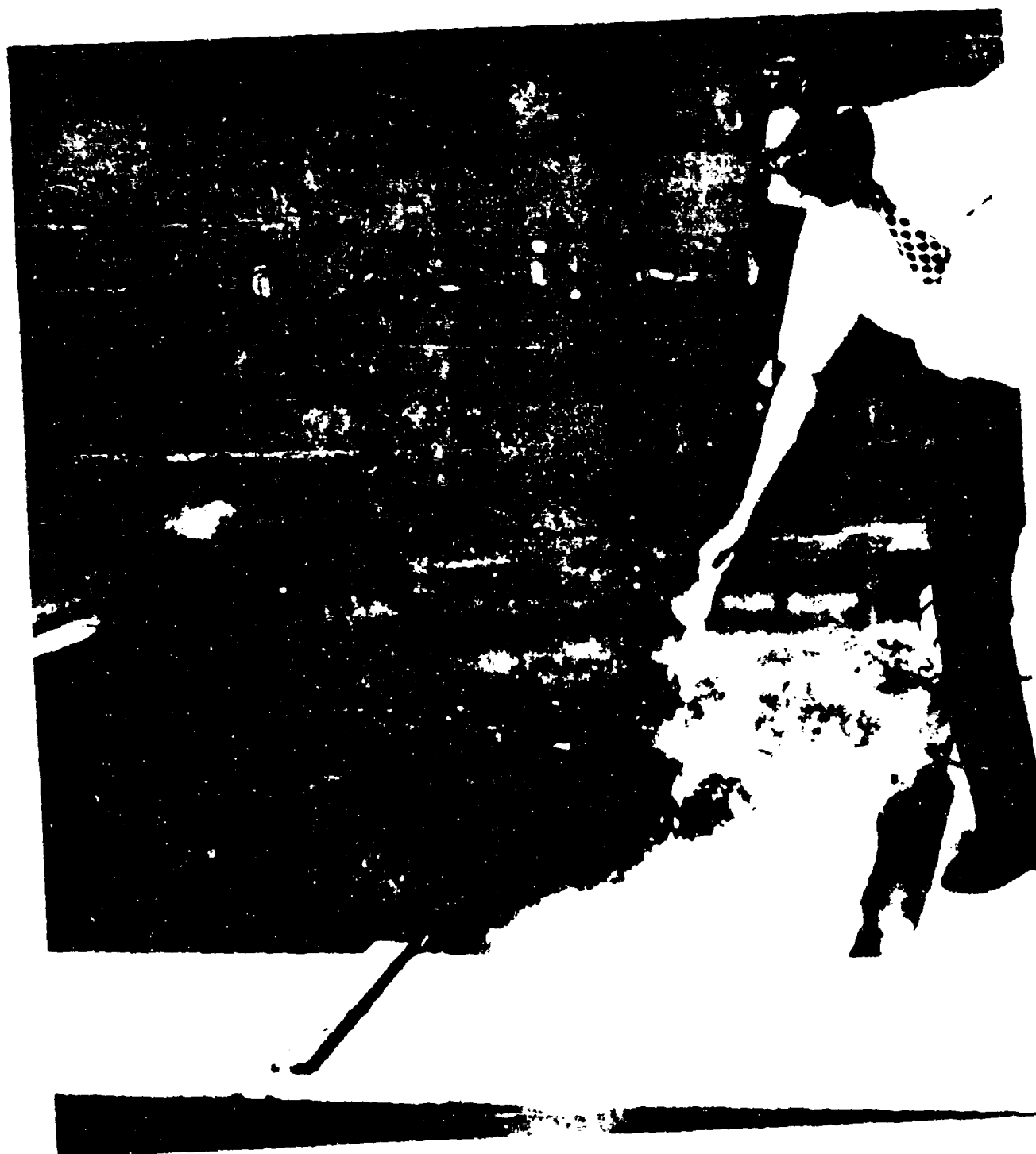


Fig. 4. Carbonation, using powdered Dry Ice sprinkled over surface of oil after spraying with Amine D solution.

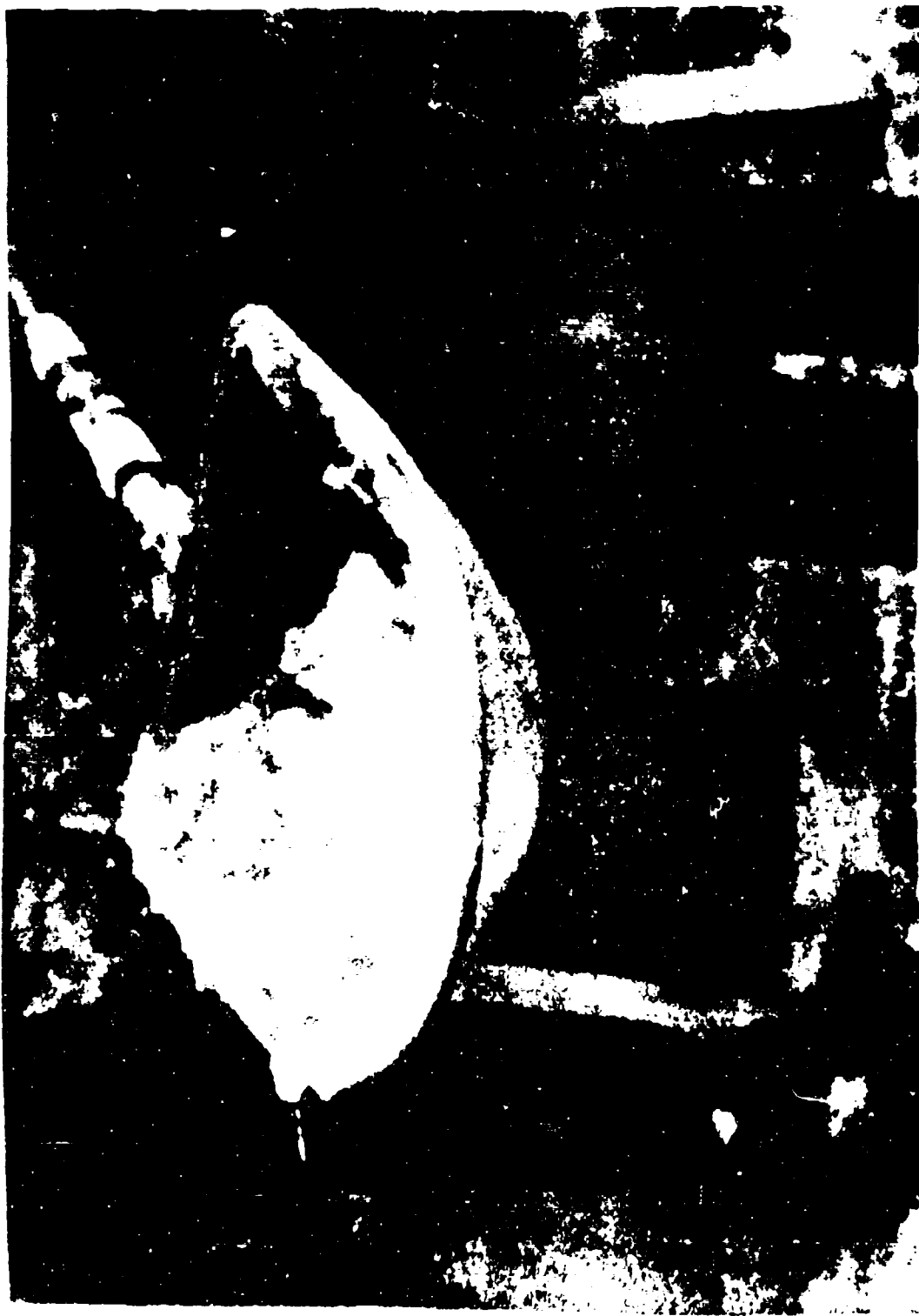


Fig. 5. Gelled fuel oil after amine spraying and carbonation treatment.
The gel consistency is sufficiently rigid to permit complete recovery by means of hand held sieves, as shown above.



Fig. 6. Another view of the gelled oil, showing the semi-rigid, lard-like consistency of the gel.



Fig. 7. Gelled oil (white lumps) together with ungelled oil (dark patches), the mixture of which has been subjected to action by Navy Piston Oil Film. This test strongly indicates that gelled oil can be "herded" in the same manner as ungelled oil by such collecting agents.

I. P. Objectives:

1. Demonstrate spraying technique and subsequent application of CO_2 .
2. Demonstrate compatibility of Amine D system with Piston Film.
3. Demonstrate sieving technique for harvesting of gelled slick.

C. Results:

1. Homogeneous application of Amine D to oil slick was achieved using the spray technique.
2. Piston Film did not interfere with subsequent application of amine or with gelation results. As shown in Figure 7 (page 21) oil when added to gelled oil was then treated with small amounts of Piston Film; both oil and gelled oil were successfully "herded" using this technique.
3. Sieving is a viable technique for harvesting of gelled oil.

II. Large quadrant test: (see Figures 8, 9 and 10, pages 23 - 25)

A. Sequence:

1. Apply 5 gallons of previously mixed No. 2 fuel oil/Amine D solution (4.1 gal. oil and 0.7 gal Amine D solution, for a 15% concentration of the amine solution, and a 10% concentration of amine).
2. Dust with powdered Dry Ice.
3. Harvest with DIP.

B. Objective: to demonstrate harvesting technique and compatibility with DIP craft.

C. Comments: premixing of oil/amine solution was necessary inasmuch as the sprayer would not reach all dimensions of the large quadrant.

D. Results:

Prior to this test, a similar test was performed using ordinary oil (dyed red for greater visibility; see Figure 8, page 23). Using the DIP, approximately 1 hour was required to recover all that was feasibly recoverable, i.e., about 90%, of the spill. As is the case in any ungelled oil situation, the tendency of the oil to drift back over cleared areas considerably complicated the harvesting of



Fig. 8. Ungelled oil (dark patches) shown drifting back in the wake of the DIP recovery craft, which is picking up oil at the bow of the vessel. This tendency of ungelled oil to drift back over cleared areas is a serious problem in recovery operations.

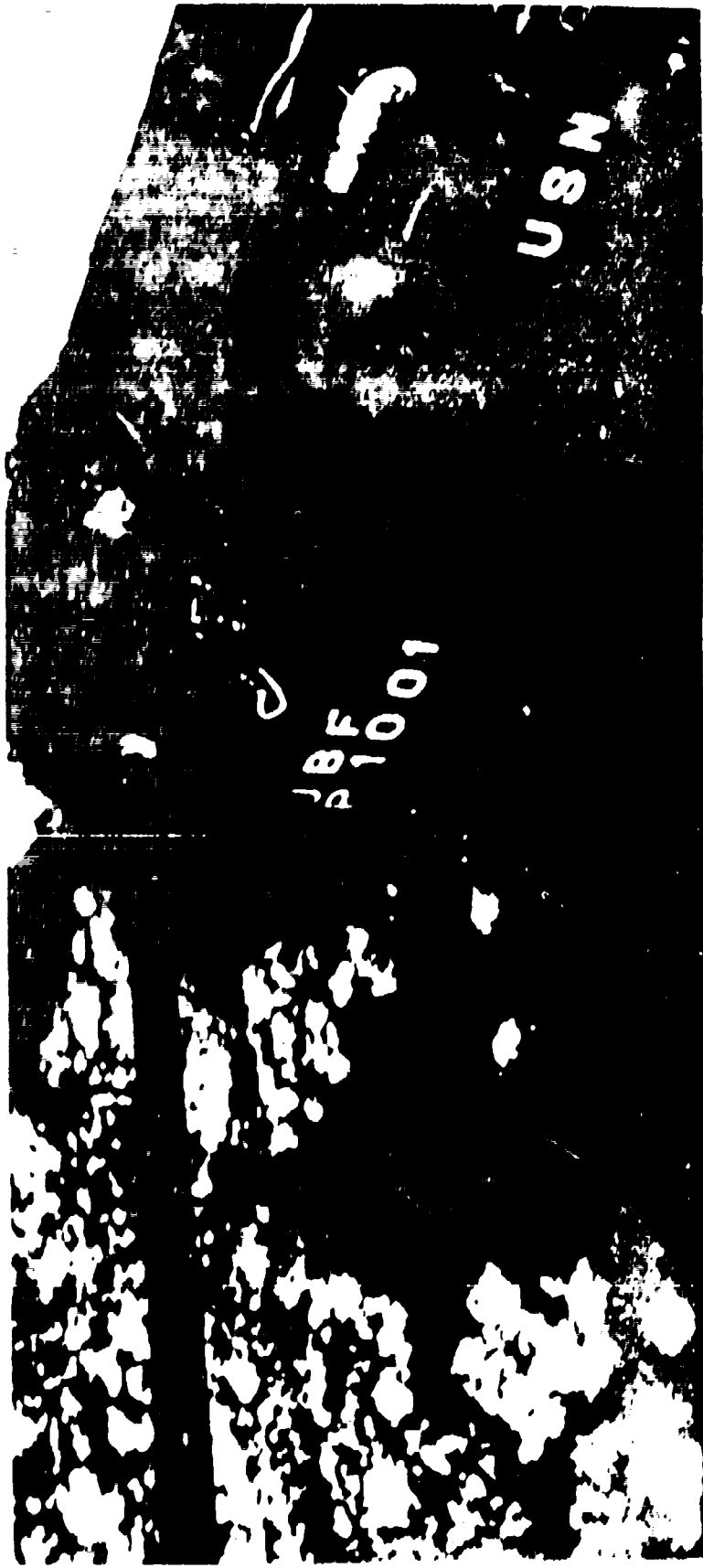


Fig. 9. Recovery operation using hip crane, which will be used by similar operations. The crane is being used to lift the body of the victim from the water.

1. The victim of the accident is being lifted by the crane. The crane is being used to lift the body of the victim from the water. The crane is being used to lift the body of the victim from the water.
2. The victim of the accident is being lifted by the crane. The crane is being used to lift the body of the victim from the water. The crane is being used to lift the body of the victim from the water.



Fig. 10. Forward view of DIP craft in process of recovering gelled oil.

meaningful quantities of the oil.

As shown in Figures 9 and 10 (pages 24 and 25), gelation of the oil renders the oil relatively immobile; there is little if any tendency for the gelled oil to drift back over cleared lanes, and little if any tendency for the gelled oil to move away as the recovery craft approaches. Moreover, the visibility of the gelled oil is very considerably enhanced, due to the white color of the gel.

ADDITIONAL OBJECTIVES AND TASKS DEVELOPED DURING THE COURSE OF THE INVESTIGATION.

In addition to the objectives and tasks discussed above, several new avenues for research efforts along the lines of the project opened up during the course and as a result of the project research. These are discussed below.

I. Reduction of volatility by gelation of hydrocarbons.

Early in our project work we observed, qualitatively, a rather marked decrease in evaporation rate of the more volatile hydrocarbons being tested, when these had been gelled, relative to the ungelled hydrocarbons. This observation was noted in our first two project reports. By correspondence dated 1 March 1976 (see Appendix E) the NRL Scientific Officer noted that such an effect could be of importance not only in terms of immobilizing spills of flammable jet fuels and gasoline, but also in decreasing the hazards (vapor and fire) attendant with such liquids, and encouragement was given to further tests along these lines.

Accordingly we devised a crude but effective volatility measuring device which provided remarkably good reproducibility in the various tests performed in this modification of a wind tunnel; see Figure 11 (page 27). Within the tunnel was placed two dishes containing equal amounts of water, on which was floated equal amounts of a given hydrocarbon, one sample being gelled with a 10% Amine D/ethyl alcohol/benzyl alcohol solution and the other sample being ungelled. A fan controlled by a variable transformer blew controlled rates of air over these samples, the wind velocity being measured by an anemometer at the other end of the tunnel. At one minute intervals the dishes were removed and weighed to determine weight loss of hydrocarbon by evaporation.



Figure 11. Volatility Measuring Device

To the left is an anemometer; the box holds two samples, one being gelled and the other ungelled hydrocarbons at equivalent positions in the wind created by the fan at the right.

Initial water temperatures were established at 20° C. (68° F); varying amounts of cooling occurred during the evaporation tests, depending on the volatility of the hydrocarbon being tested; as would be anticipated, the ungelled samples cooled more than the gelled samples, which underwent less evaporation. On this basis, if constant temperatures had been maintained, it would be anticipated that the ungelled samples would evaporate even more rapidly than the gelled samples, than was observed in these tests.

Using a pure volatile hydrocarbon, cyclohexane, and with a wind velocity of 707 feet per minute (about 7.5 knots), a loss of 18.0 g. of ungelled cyclohexane was experienced in 17 minutes, compared to a loss of only 5.8 g. of gelled cyclohexane in this same amount of time. With AVGAS 145, ungelled AVGAS evaporated almost exactly twice as fast as did gelled AVGAS.

J. Reduction of flammability by gelation of hydrocarbons.

Based on the foregoing investigation of volatility effects, it was attractive to investigate the possibility of reduction of flammability.

Our initial studies tended to indicate that very drastic decreases in flammability, far more than should have been anticipated (from this position of hindsight), were being afforded by gelation of materials such as gasoline.

As an example, in the test operation at the JBF facilities on 20 - 21 September 1976 (see Appendix D), the following scenario was proposed:

III. Flame suppression test:

- A. Apply 1 mm film (75 ml) of ungelled gasoline to surface of 10 ft x 1" (deep) x 1" (wide) trough filled with water.
- B. Ignite downwind end of trough and time spread of flame down trough.
- C. After fire has burned out, apply 75 ml of 85% gasoline - 15% Amine D solution to trough. Dust with powdered Dry Ice.
- D. Set fire to downwind end of trough; gelled film probably will not ignite or will burn very slowly down length of trough if ignition does occur.

As set up, the scenario worked perfectly: the ungelled gasoline burned readily, requiring about a second or less to sweep down the trough; and the gelled gasoline did not burn at all, even when pieces of the gel were exposed to a blowtorch flame while in the trough (although, when removed from the surface of the water, slow burning did occur).

Imbued with the success of this experiment, the Principal Investigator then repeated the experiment using a little over 200 ml of gasoline-Amine D solution, thereby providing a 3 mm film of gelled gasoline after treatment with the Dry Ice. On applying a match to this trough experiment, the gelled gasoline burst into flames which rapidly spread down the trough.

The NRL Scientific Officer, Dr. Garrett, suggested a probable reason for the anomalous behavior, this being that thin films of gasoline (ca. 1 mm thick) over water burn less readily, apparently due to heat exchange into the water, than do thicker films of fuel.

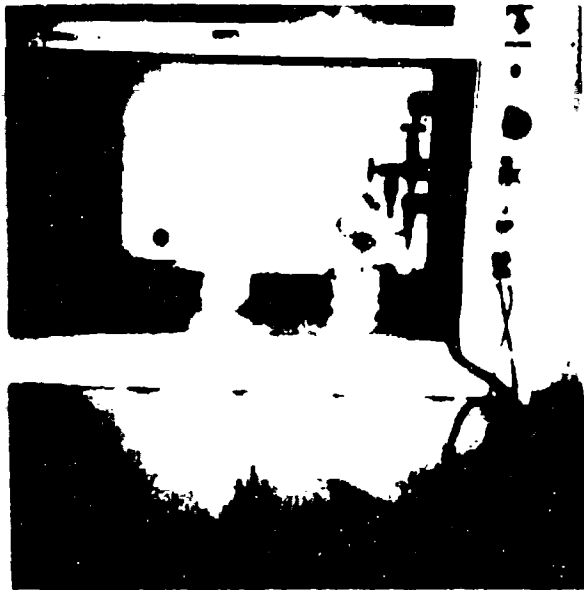
It should be noted that the 1 mm film of gasoline (ungelled) did burn, and the 1 mm film of gelled gasoline did not; this in itself could suggest that thin films of volatile flammable fluids might be gelled, feasibly, to suppress ignition. Moreover, a series of tests performed subsequently on a laboratory scale (see Figure 12, page 30), indicate that perhaps gelled fuels burn more slowly with less intensity than do ungelled fuels. Finally, the decreased volatility of gelled hydrocarbons suggests that the flame hazard in terms of nearby sources of ignition could be significantly reduced by gelation; future work along these lines is proposed in the next section, dealing with "Recommendations for Future Work".

K. Ultraviolet fluorescences as a means of enhancing visibility of gelled and ungelled oil slicks.

This work was not carried to a completion in terms of obtaining fully quantitative results. The results were promising enough to indicate that further work should be performed; again, this will be discussed in the next section.

Using a sample of a bottle labeled "Venezuelan Crude Oil" found in one of the store rooms at this University, a thin slick of the oil was applied to a small pool, and the slick illuminated by both short and long wavelength UV (254 nm and 366 nm). Some fluorescence was noted at the long wavelength illumination, but probably not enough for operational use. No. 2 Fuel Oil and similar refined, distilled stocks yielded even less fluorescence, though there was some in every instance.

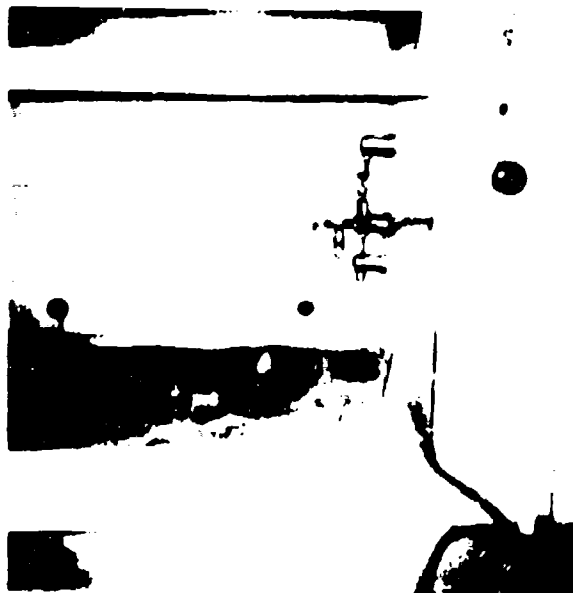
Figure 12. Flame tests:



A. Dish at left contains ungelled gasoline, burning with greater intensity than the gelled gasoline in dish to right.



B. Ungelled gasoline in dish at left is beginning to burn out; gelled gasoline is burning more slowly.



C. The ungelled gasoline has burned out; gelled gasoline continues to burn.

It was found that application of an oil soluble fluorescing agent (e.g., oil soluble Rhodamine B) in minute quantities produced, as would be expected, very visible fluorescence even with the low level long range UV light source which we utilized.

CONCLUSIONS

Laboratory tests indicate that a solution of 70% Amine D, 15% ethyl alcohol and 15% benzyl alcohol when applied to a concentration of about 10% to oil slicks gave excellent gelation of the oil after treatment with powdered Dry Ice. With the exception of Navy Residual Special Fuel Oil #6, all hydrocarbons tested were successfully gelled; these included a variety of pure hydrocarbons and such important mixtures as JP-5, AVGAS 145, No. 2 Fuel Oil, Diesel fuel, and similar items of commerce. Film thickness does not appear to be a significant factor; high water temperatures (above 80° F.) gives poor results for some hydrocarbons, but over most operational temperature spans temperature does not appear to be important, nor does salinity. Larger scale field tests confirm these results, and indicate that gelation of hydrocarbons by this process offers very significant advantages in the recovery of the floating oil slick. This is particularly the case in terms of the ease of pick-up of the gelled oil; the immobilization of the oil, which tends to keep the slick from drifting back over previously cleared areas; and the greater visibility of the gelled slick. Oil gelled in this manner can be very easily harvested using conventional DIP craft or even by nets or sieves, manually operated.

There is a low order of toxicity associated with the use of Amine D, in terms of exposure of marine organisms; however, this is of the same order of toxicity as is that of the oil slick in which it would be distributed; with water depths of more than two feet, the toxicity problem is negligible.

There is a significant (ca. 50%) reduction in evaporation rate of gelled, compared with ungelled hydrocarbons. This factor would be important in terms of reduced vapor hazards and perhaps fire hazards.

Ultraviolet fluorescers as additives to the gelling agent or to the oil slick itself were studied and found to have promise in terms of providing increased visibility for nighttime operations.

RECOMMENDATIONS FOR FURTHER WORK

Based on the results of this investigation, the following topics appear worth of further research and development:

1. Field test at sea or in open harbor, using the technology developed in this investigation.
2. Design and manufacture of prototype equipment for use in DIP craft for application of amine and CO_2 to oil slicks.
3. Development of a solubilized Amine D carbamate (i.e., Amine D pre-treated with CO_2), thereby obviating the requirement for Dry Ice or other means of carbonating the Amine D after it has been applied to the slick.
4. Use of a hydrogenated derivative of Amine D (whereby the aromatic ring would be reduced to a cyclohexane ring) which could be expected to a lower freezing point and lower toxicity than the Amine D itself.
5. Further study into the possibility of using Amine D or other amine gelling agents to reduce volatility and vapor and fire hazards posed by volatile hydrocarbon spills.
6. Use of fluorescing agents to improve visibility of gelled or ungelled oil slicks.

Research proposals based on these concepts are being prepared for submission for consideration.

APPENDIX A

ACUTE TOXICITY OF HERCULES AMINE-D

(Prepared by Sias Research Laboratory, Iahey Clinic Foundation)

Note: Some of the pages of this Appendix are independently numbered, or have no page numbers. Collectively, these pages comprise pages 33-42 of this overall Report.

Acute Toxicity of Hercules Amine-D

In an attempt to determine the nature of the toxic substance or substances in Amine-D and #2 fuel oil mix, several experiments were conducted. Using the barrier tank apparatus described in our previous report (see attached), one ml aliquots of #2 fuel oil with 3% ethanol added were mixed with artificial seawater to make up one liter final volume. Any one of five Fundulus heteroclitus taken from the holding tank was checked at random for normalcy and the other four were placed in the test tank. At the end of two hours the fish were sacrificed, and blood from the caudal artery was analyzed electronically. Standard slides for microscopic evaluation were also made. Differential blood counts and photomicrographic images were prepared from each slide. Figure (13) shows a photomicrograph taken of a blood slide from a control sample fish (swimming in a barrier tank in one liter of artificial seawater. Figure (14) shows the change in the blood cell population of F. heteroclitus subjected to 970ppm of #2 fuel oil in artificial seawater for 2 hours. Our previous work showed that F. heteroclitus specimens were able to withstand 5-10ppm of Hercules Amine-D (solubilized with 3% ethanol) in artificial seawater for 24 hours without exhibiting any untoward reactions, and that they could withstand the mix of the Amine-D, ethanol and #2 fuel oil in low concentrations 10-20ppm in artificial seawater for 24 hours. In this latter case, however, the electronic monitoring showed that the blood cells had been altered. In our final experiments, therefore, we stressed the system and looked at the acute toxic effects of the Amine-D/ethanol and the Amine-D/ethanol plus #2 fuel oil mix in 688ppm concentration and 56ppm concentration respectively.

Differential blood counts done on all samples showed that the erythrocyte: lymphocyte: thrombocyte: granulocyte ratios did not change significantly. The electronic patterns and the optical microscope observations showed that the erythrocytes were effected, moreover, fish on both sides of the barrier which keeps the insoluble chemicals available to only one half of the fish in the

sample were effected similarly, thus indicating that the toxic chemical or chemicals are seawater soluble.

Table 1 summarizes the survival data and the chemical insults that test populations of F. heteroclitus were subjected to. Amine-D was added directly to the blood of F. heteroclitus as a second type of control. Amounts of Amine-D in saline ranging from 33ppm to full strength were used. All blood cells were altered regardless of the concentration, however, the effect was similar to the results seen in Figure (14), viz. an elongation of the blood cells with little or no cell membrane damage.

Acute toxic reaction in fish swimming in artificial seawater containing ethanol, Amine-D alone or in combination with #2 fuel oil effected the blood cell membrane in a manner similar to that seen in chronic copper (II) toxic reactions. The surface of the membrane loses its selective permeability and spots appear fairly evenly distributed over the cell surface. A difference between the two reactions does exist. In the case of the Amine-D reaction, the ratios of the formed elements in the blood do not appear to change. This indicates that the mechanism of action is different from that seen in F. heteroclitus subjected to copper (II) ions. The lethal interval also is interesting for Amine-D toxicity because it suggests (when combined with earlier data) that the soluble toxin is in the Amine-D and may be a contaminant. We have a minimum of information sufficient to relate the lethal interval to the Amine-D concentration regardless of whether the amine is combined in a gel, in a free mix with #2 fuel oil or solubilized in a small amount of ethanol follows a relationship which can be predicted from Graph (1). Amine-D concentrations of less than 20ppm appear to be able to be handled by the fish as easily as the fuel oil itself and, in fact, cause alterations in the blood similar to that seen in Figure (14).

If, as we conclude from the data, it is a soluble contaminant in the Amine-D

that is causing the observed toxic response, then further testing will prove the fact. Regardless of the toxin, however, in Amine-D concentration levels of 20ppm or less can be accepted as safe. The concentrations of Amine-D used to incorporate into an oil spill at sea will be mixed with a volume of water sufficient to lower the concentration of the toxin to a safe level at less than 2 feet below the seawater surface even under the condition of no mixing.

TABLE I

Reference Figure	Lethal Application (min.)	TEST ENVIRONMENT				RANDOM 300 COUNT OF BLOOD SAMPLES			
		Artificial Seawater (ml)	Number 2 Fuel Oil (ml)	Hercules Amine-D (ml)	Ethanol (ml)	Erythrocyte	Lymphocyte	Thrombocyte	Granulocyte
1	--	1,000	--	--	--	293	2	5	--
2	--	999	0.97	--	0.03	292	2	6	--
3, 4, 5	100	999	0.92	0.056	0.024	293	3	3	1
6, 7, 8	30	999	--	0.688	0.312	290	3	7	--

Graph 1. Lethal interval for Pueria heteroclitus
 subjected to acute insult of Amine D (TM, Hercules, Inc.)
 in sea water.

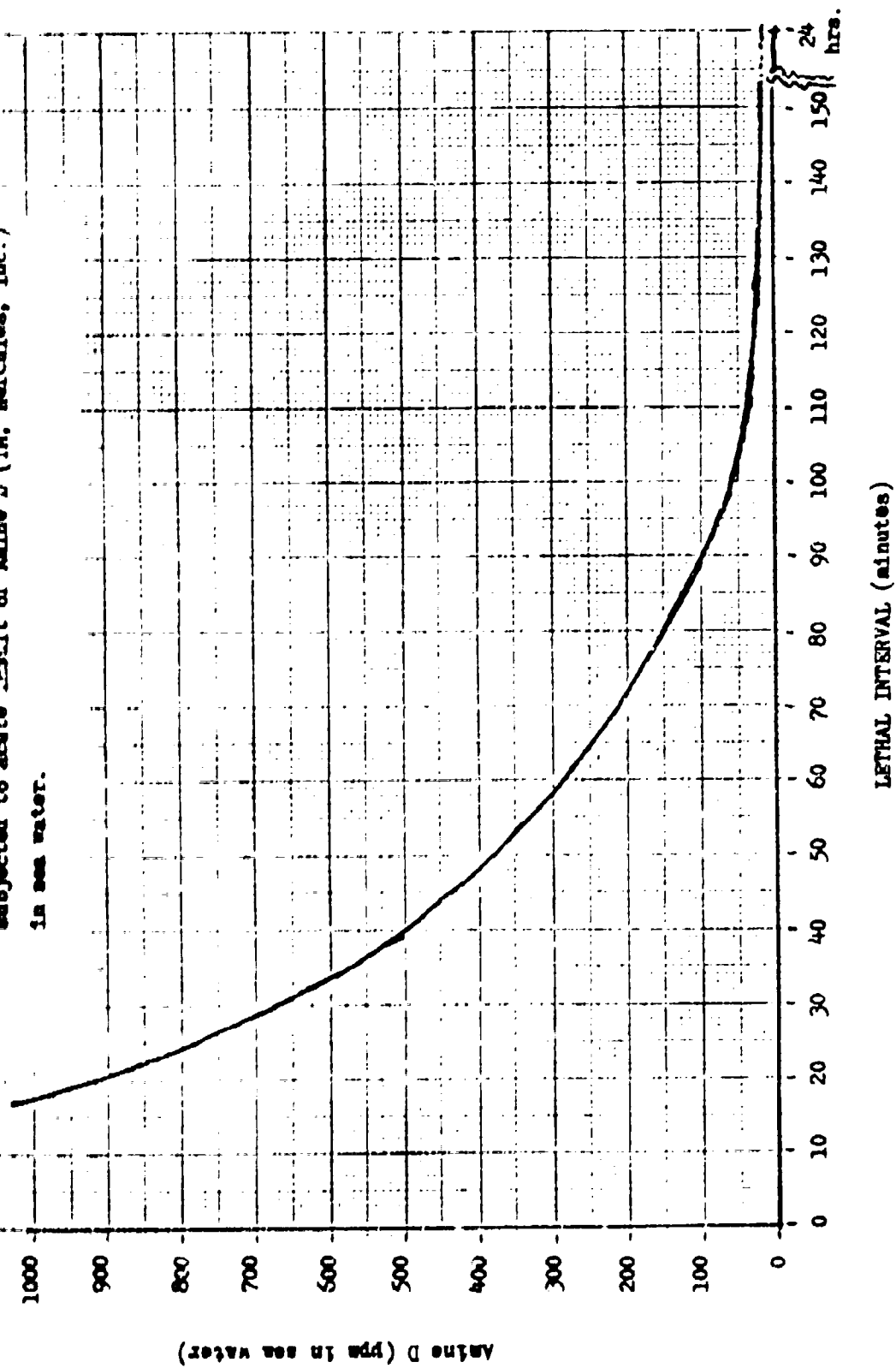




Fig. 13. Normal red blood cells show the characteristic elliptical shape and smooth, rigid membrane. Nuclei in these cells are not as clearly defined as those in the experimental cells.



Fig. 14. Red blood cells from fish exposed to the 0.1% TBM mixture show large deviations in cell width, with most cells being much narrower than normal.



Fig.15. Nuclei appear to project from the cells (A) and shedding of the cytoplasm (B) is evident.

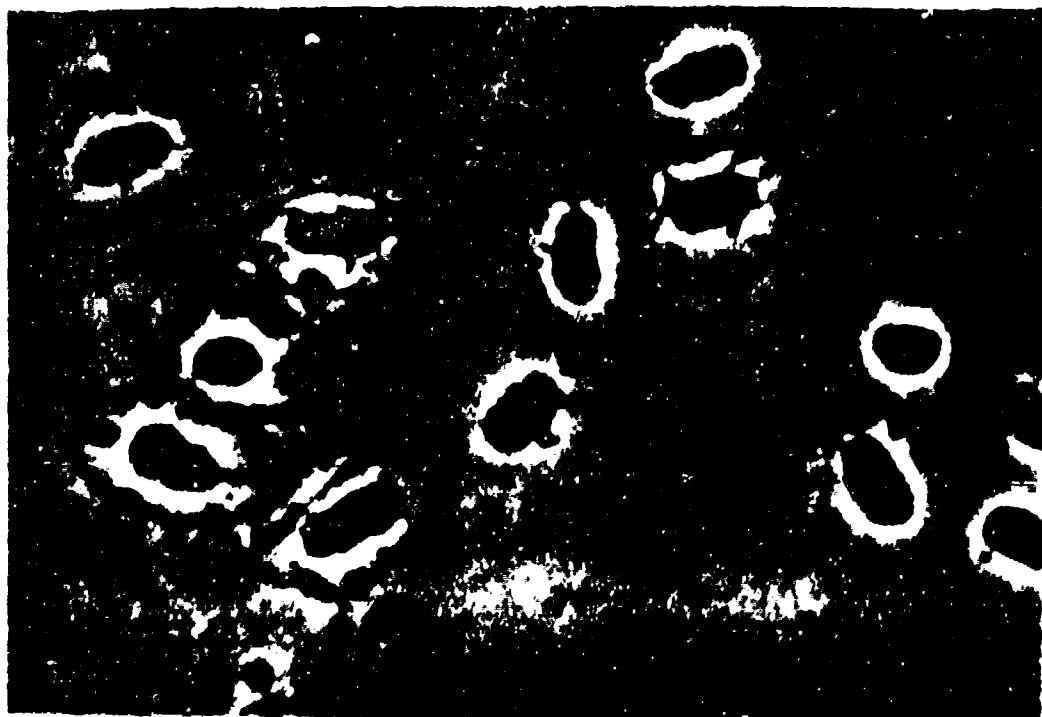


Fig.16. Isolated nuclei (A) of red blood cells; some cells show a loss of cytoplasm exhibited by clearing rings (B) around nuclei.



Fig.17. Cytoplasmic membranes show breaks and loss of rigidity (A) in RBC's from the oil, amine-D/EtOH experiments.

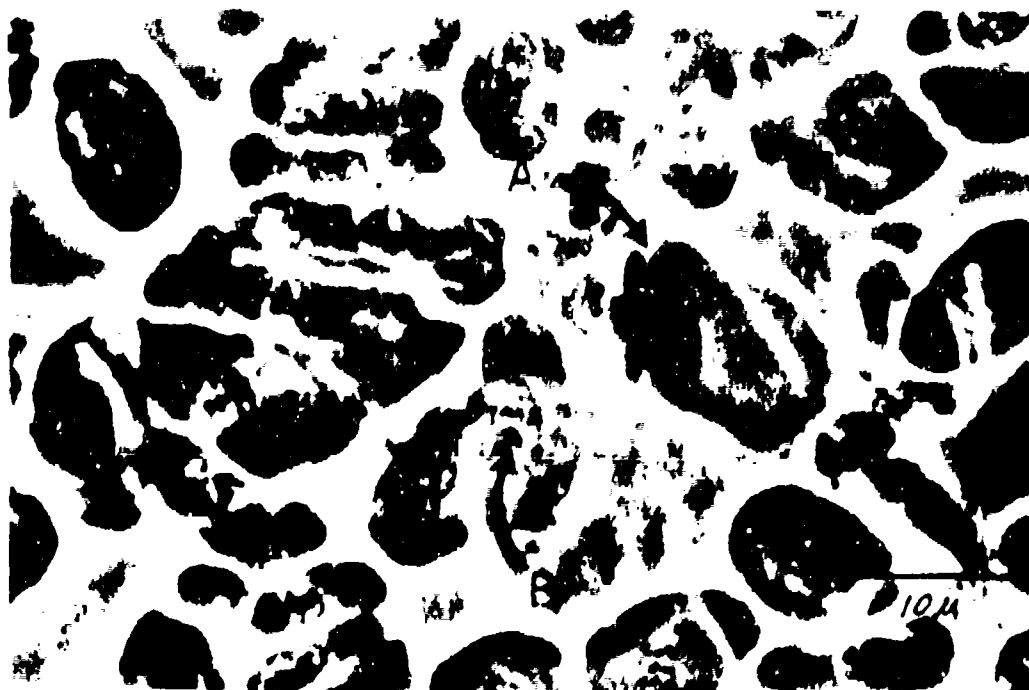


Fig.18. Red blood cells from fish exposed to amine D/EtOH show a loss of rigidity of the cytoplasmic (A) and nuclear (B) membranes, folds and projections of the membrane (C) pseudopods (C).



Fig. 19. Cytoplasmic membranes take on a vesicular shape as the projection begins to develop.

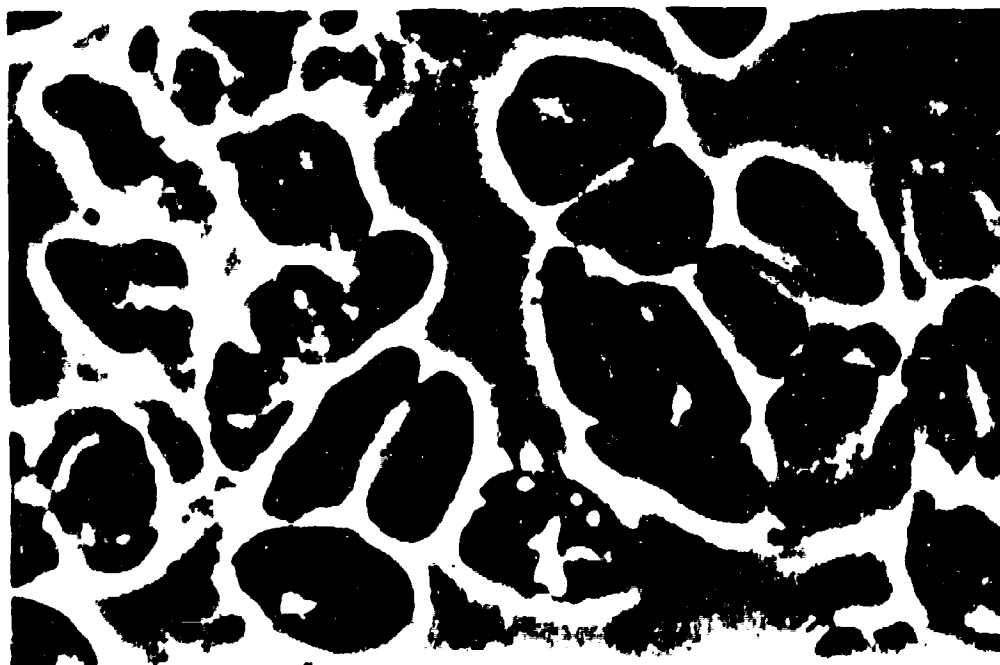


Fig. 20. Vacuoles or engulfed particles appear (possibly taken up by pinocytotic action).

APPENDIX B

TEST PLAN FOR EVALUATING AND DEMONSTRATING
JBF OIL SKIMMERS IN BOSTON HARBOR

(Prepared by JBF Scientific Corporation)

Note: Some of the pages of this Appendix
are independently numbered or have
no page numbers. Collectively,
these pages comprise pages 43-60
of this overall Report.

JBF SCIENTIFIC CORPORATION

**TEST PLAN FOR EVALUATING AND DEMONSTRATING
JBF OIL SKIMMERS IN BOSTON HARBOR**

The conditions which will be fulfilled by the test plan will be in accordance with Section 110.8 of Title 18 of the Code of Federal Regulations as follows:

Paragraph 1. c. The purpose for discharging oil into the navigable waters of Boston Harbor is to establish better methods and procedures for operating in actual oil spills so that more rapid and efficient methods can be utilized. The results of the work will be published by the U. S. Navy and American Petroleum Institute. Copies of these reports are distributed throughout the country. A copy of each report generated will be given to EPA so that the information can be further distributed. Finally, JBF will publish the results in technical papers which will be presented at national and international oil pollution conferences. Without tests which discharge oil, it would be impossible to develop the type of information needed to improve the state of the art.

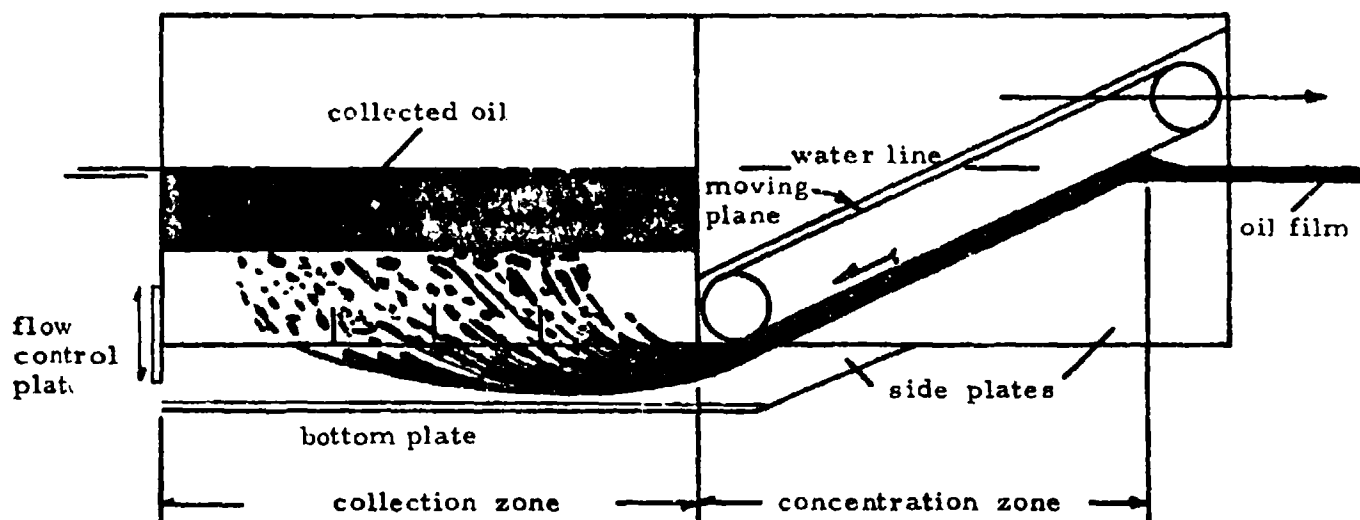
Paragraph 1. d. JBF Scientific assumes all liability for any personal injury, property losses or environmental damages results in directly or indirectly from any testing or demonstration program, and for all costs, including costs or damages resulting from cancellation by the Administrator or failure by the Administrator to cancel tests and demonstrations.

Results of any testing or demonstration program shall be made available to the Administrator.

Paragraph 2. a. The work plan for the tests and demonstration proposed is contained in the following sections.

(1) Description of Equipment to be Tested

Four models of JBF Skimmers will be tested during the period August 1, 1976 through July 30, 1978. A description of the concept and of the individual models that will be tested are shown on the following pages.

THE DIP CONCEPT

Dynamic Inclined Plane (DIP)* skimmers are based upon the concept of collecting the oil under the surface of the water, thus greatly reducing the effect of waves. As the skimmer moves through the water, or the water moves past the skimmer, the oil is forced to follow the surface of a moving inclined plane to a collection well underneath the skimmer. Buoyant forces cause the oil to surface in the well, forcing water out the bottom. As the oil collects, it is pumped off to storage tanks. Separation occurs automatically and virtually no water is collected.

The moving plane is a heavy-duty conveyor belt which carries oil and sorbents down to the collection well. Recovery is in excess of 90% of the oil-sorbent mixtures presented to the skimmer mouth, in one pass of the unit and in the presence of waves. A set of rigid articulated sweeps is also available for attachment to the bow of the skimmer. These sweeps increase the "effective mouth width" and, hence, the oil collection rate by a factor of three.

Unique features of the DIP skimmers include:

- the ability to harvest any floating material, including debris and sorbents, without changing the skimmer configuration
- automatic oil/water separation so that the recovered oil is virtually water free. No water is added by the pickup process.
- a rugged, long-life belt, that uses natural forces to transport the oil to the collection well. No absorbent, or flow-through, principles are required.
- skimming may be performed at speeds, or in currents, between 0 and 3 knots
- excellent performance in waves since the oil is collected under the skimmer

*Patents pending

JBF SCIENTIFIC CORPORATION

DIP 1000 SERIES

These units were designed for use in restricted environments, under piers and between nested ships, in either a moving or a stationary mode. They are effective harvesting oil inside a containment boom, as a link in a boom, or operating outside the boom.

The units contain twin propulsion, a moving plane, a collection well, and a pump to transfer the oil from the skimmer to the pier. A 25-foot long wand is used to guide the skimmer through the slick and the oil is pumped ashore through the same wand. A remote control box provides the capability of turning the belt, pump, and propulsors on and off. These units are air operated.

DIP 2000 SERIES

This series of skimmers is designed to be used in either a sweeping or stationary mode. They are highly rugged, portable, and can be trailered and launched quickly. They can be moored in a river or bay, where wind and current bring the oil to the skimmer, or strapped to the side of a vessel of opportunity and used in a sweeping mode. When operated with a support vessel, they are effective in 3-foot waves. Units are available with either electric or diesel power.

DIP 3000 SERIES

This series fills the need for a general-purpose, fully self-contained skimmer to recover a wide range of floatables under conditions typically encountered in calm and rough waters. The units are diesel powered, twin screw, and all pumping, propulsion, and belt functions are hydraulic.

DIP 3001 units are 25-foot long and have a total onboard storage capability of 1400 gallons. Operation is highly effective in waves to several feet and at speeds to 3 knots.

The DIP 3003 is larger than the 3001 and is designed to operate in more severe wave environments. It is 35-foot long, has a deeper draft, larger freeboard, and can store 4000 gallons of oil on board.

DIP 4000 SERIES

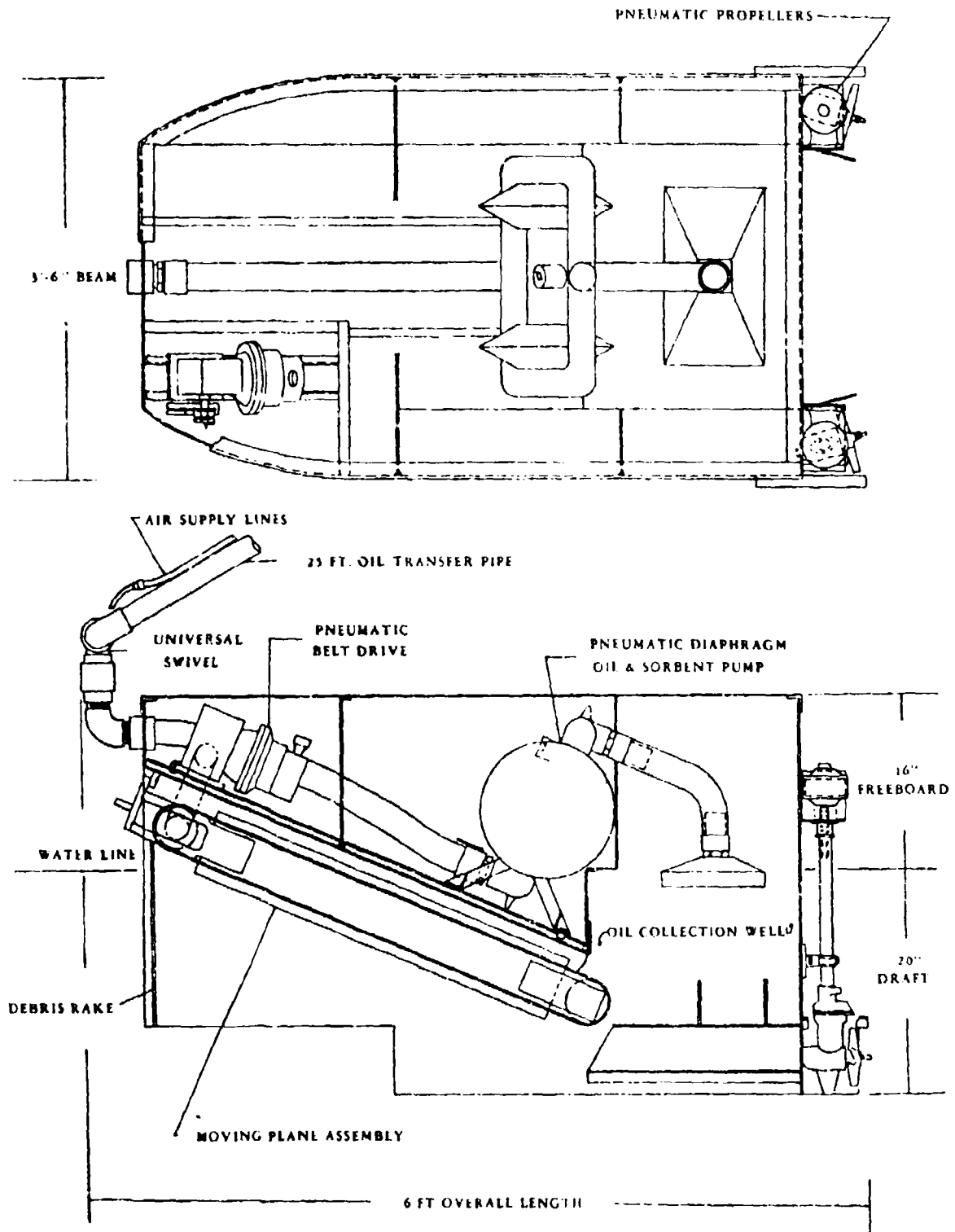
This series of skimmers has been designed primarily for unmanned skimming in high waves.

The DIP 4001 is a 26-foot long, diesel-hydraulic, skimmer that can be operated manned in low sea states and unmanned in high seas. In the unmanned configuration, the skimmer is towed astern and to the side of a large support vessel. An umbilical between the skimmer and the support vessel is used to transmit control signals to the skimmer and to pump recovered oil from the skimmer to the support vessel for storage.

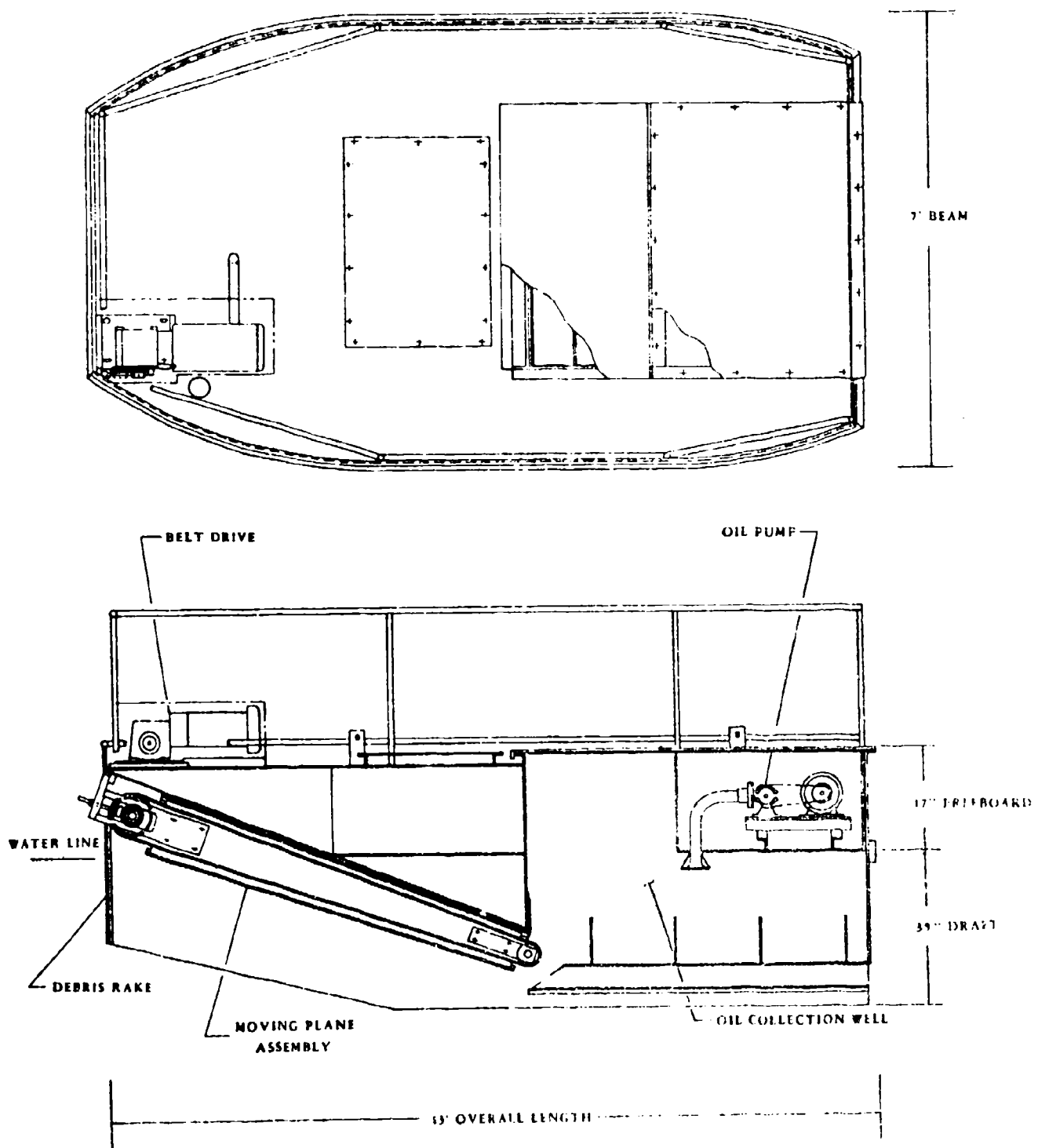
The skimmer can actively (under power), or passively (rudder only), change its position, with regard to the support vessel, to allow the skimmer to follow the edge of a slick or a long windrow.

JBF SCIENTIFIC CORPORATION

DIP 1001

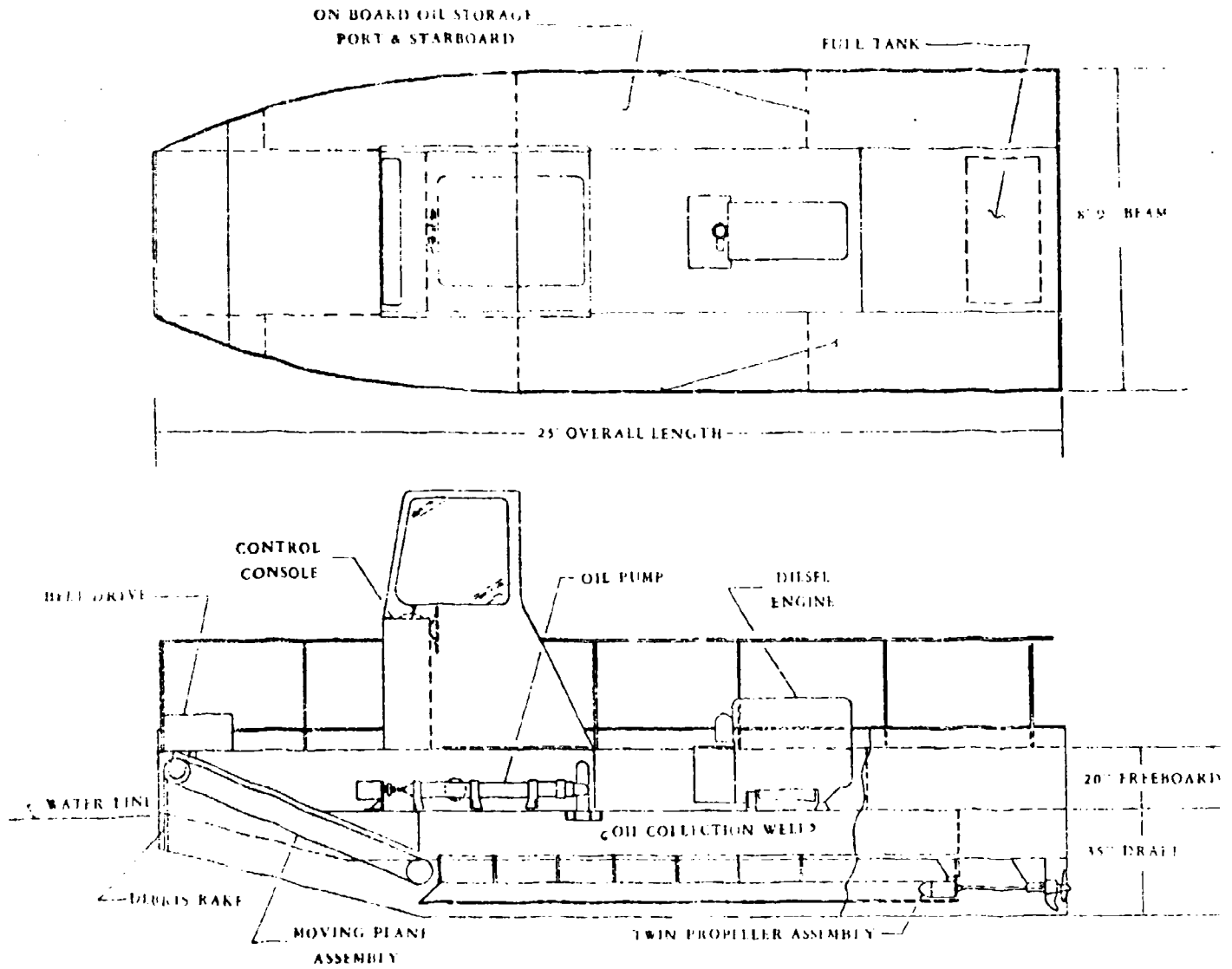


DIP 2001

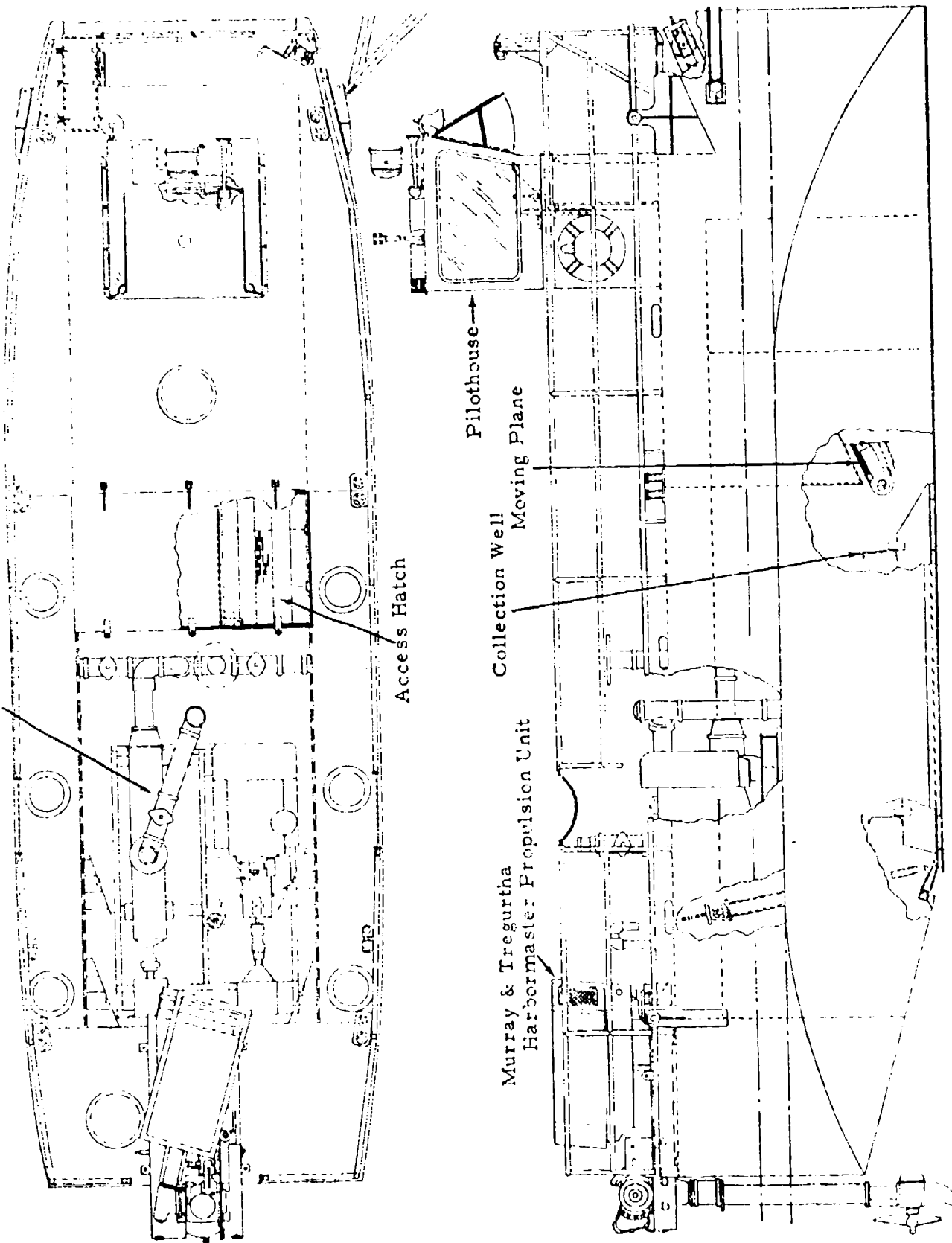


JBF SCIENTIFIC CORPORATION

DIP 3001



450 GPM Pump and Diesel Arrangement



Arrangement of the DIP 3003

Types of Oil to be Discharged

Soybean Oil

Soybean oil will be used to simulate the light fractions, like No. 2 fuel oil. It is a biodegradable natural oil which has been used in oil boom evaluations by Johns Manville and the U.S. Coast Guard off the coast of Florida. It was selected by Johns Manville and approved by the federal and local authorities because it was determined to be virtually harmless to the environment.

Caster Oil

Caster oil is also biodegradable, because it is a natural oil. It is used for medicinal consumption in the human body and is readily digestible in animals. Although it is much more expensive than soybean oil, it is selected because its properties are much closer to those of the residual oils.

Sorbents and Natural Floatables

Sorbents will be used to determine the effectiveness of the various units when used with nontoxic sorbents. Typical sorbents that may be used are polyurethane foam, Ekoperl, straw, and seaweed.

Piston Films and Gelling Agents

These chemicals are for the purpose of reducing the interfacial tension between oil and water, thus preventing the rapid spreading of oil. They are also used to control the oil slick by spraying very small amounts around its periphery. Chemicals of this type will have already been approved for use by the Environmental Protection Agency. Amounts used shall not exceed 2 gallons/linear mile at 6 hour intervals and shall not be applied more than 3 times in a 24 hour period.

Fuel Oils

Distillate and residual fuel oils and various mixtures of each will also be used in small quantities under carefully controlled conditions. The main purpose of using these oils will be to establish the validity of the tests performed with the simulants.

Quantity of Oil, Method of Discharge, and Number of Tests

There will be several test situations evaluated. These will include tests in boomed-off areas, tests where the oil is deployed immediately ahead of the unit, and tests of free slicks. The free-slick tests, however, will be run with sorbents, straw, and seaweeds mixed with very small quantities of biodegradable oil (approximately 5 gallons).

Oil Tests in Boomed-Off Areas

Tests in boomed-off areas will be performed by completely enclosing an area within a boom. The floatable will be within the area, beginning with very small quantities (5 gallons) and increasing gradually to approximately 25 gallons. The small quantities will be used to determine the effectiveness of completely cleaning up that particular floatable. Larger volumes will be used to obtain quantitative information only after it has been determined that the system does do a good cleanup job. Several tests that were run with the DIP have shown that this procedure is reasonable. The location of these tests will be between piers at the old South Boston Naval Shipyard (Annex). No more than a total of 100 gallons of biodegradable oil and 100 gallons of petroleum oil will be spilled for all of these tests and no more than 50 gallons of either type will be spilled within a 24 hour period. All discharges will be made in the morning hours so that there is ample time for cleanup operations before dark.

Harbor Tests of Oil Recovery in a Skimming Mode

Skimming mode tests with the skimmer underway: The floatable will be distributed on the water surface immediately in front of the unit between sweeps or confinement arms. These types of tests were run with the early EPA Demonstrator, where small amounts of oil were deployed and harvested. If piston films and gelling agents prove to be effective, these films will be used as aids to confine the floatable to narrow slicks. Petroleum oils will be tested primarily to establish the relationship between the biodegradable and petroleum oil tests. This general approach was successfully applied in the tests on the EPA Demonstrator. The location of these tests will be between the piers at the South Boston Naval Shipyard (Annex) as indicated on the map. No more than 25 gallons of oil will be spilled/test/day. |

Tests Between Piers

Tests between piers at Pier 6 of the old Shipyard Annex are anticipated in August of 1976. These tests will involve the use of fuel or soybean oil mixed with seaweed and debris in the form of wood and natural stringy materials. There would be a total of 6 tests performed at 25 gallons per test with no more than two tests being performed per day.

(2) Assessment of Environmental Damage

The total quantities of oil spilled are less than the maximum stated in the EPA guidelines. Practically all of the oil will be removed by the skimmers being tested. Based on the quantity of oil that will be spilled and the efficiencies of the devices which will be skimming, less than 10% of the test oil will be remaining in the water. This amount will not exceed a maximum of 2.5 gallons in a 25 gallon test. Within 24 hours less than 5 gallons would be remaining in the water. There will be no environmental damage associated with this quantity of oil.

(3) A copy of this document is being provided to the U.S. Coast Guard. Immediately following each test, all test oil regardless of type will be picked up off the water surface. Cleanup procedures will be performed using JBF skimmers in combination with sorbents that have been demonstrated previously. All oil mixtures will be picked up and collected in the skimmer collection chambers. The concentrated mixture will then be transferred from the well to onboard storage of a unit or to a support vessel.

(4) Contingency for all Tests

To eliminate the possibility of causing any damage to the environment while testing with oils, the amount deployed for each test run will be limited to 25 gallons. At no time will more than 50 gallons of oil be spilled within a 24 hour period for the types of tests described in the section entitled "Harbor Tests of Oil Recovery in a Skimming Mode". Based on efficiencies measured at EPA's tow basin in New Jersey for the DIP skimmer USN DIP 3001, 90% of all the oil will be recovered in the first pass (see Table I attached). Assuming several passes, much less than 10% will be remaining in the water. Deflection booms will be critically located downwind or down current to insure that none of the oil spilled by accident will be allowed to escape into open water.

Period of Test Performance

Based on approval by EPA, tests will begin in August of 1976 and will extend into July of 1978. EPA, the U.S. Coast Guard, and the Massachusetts Division of Water Pollution Control will be notified by telephone at least 24 hours in advance of all major tests performed in Boston's waters. Point of contact with the Coast Guard will be the Oil Pollution officer at the COTP Base Office.

(5) Technical Justification

These tests which are required in our contracts with the University of Lowell, the American Petroleum Institute, and the U.S. Navy will improve the state of the art and provide much needed technical data to improve the design of future oil recovery systems and develop more efficient methods for recovering oil spills.

JBF SCIENTIFIC CORPORATION

USN DHP 3001 Oil Recovery System Tests

Table I. Throughput Efficiency 1 - 2.5 knots
(Free Slick - Skimmer Aperture \approx 5 feet)

Test No.	Tow Speed (knots)	Belt Speed (knots)	Back Plate Opening (inches)	Throughput Efficiency* (%)	Average Throughput Efficiency* (%)
1	1	1	0	97	
2	1	1	0.5	101*	
3	1	1	2	94	
4R	1	1	3.5	95	
1 KNOT AVERAGE					97
64R	1.25	1.25	3.5	94	94
9	1.5	1.5	0	103*	103*
82	1.75	1.5	0	99	99
60C	2	1.75	3.5	93	93

Throughput Efficiency = $\frac{\text{Oil Collected}}{\text{Oil Intercepted}}$ in One Pass

*Standard Deviation of Volumetric Measurements of Collected Oil Based on 13 Calibration Runs is \pm 6%.

JBF SCIENTIFIC CORPORATION

(6) Provision for Technical Documentation

Technical information that is obtained will be provided to EPA and all other federal and local agencies that request it.

(7) Concurrence of State Authority

A copy of a letter from the Commonwealth of Massachusetts for similar tests in previous years is appended.

(8) Prior Notification to the U. S. Coast Guard

The attached form will be sent to the Coast Guard notifying them of any test in excess of 20 gallons. The Coast Guard will be notified by telephone of all tests to be performed in Boston Harbor regardless of the quantity of oil to be spilled.

NOTIFICATION OF TESTS



SCIENTIFIC CORPORATION

2 Jewel Drive

Wilmington Mass 01987

Tel (617) 657-4170

Date: _____

U.S. Coast Guard
First Coast Guard District
427 Commercial Street
Boston, MA

Attn: Pollution Control Officer

Gentlemen:

This is to notify you that JBF Scientific Corporation will be performing:

- A. Tests in a boomed off area
- B. Tests in a free skimming mode

Date of Tests: _____

Total quantity of oil to be spilled within a 24-hour period: _____

Quantity per test: _____ Number of tests: _____

Location: _____

If there are any questions concerning the above tests, please contact
Mr. Ralph A. Bianchi at 657-4170.



THE COMMONWEALTH OF MASSACHUSETTS
WATER RESOURCES COMMISSION

LEVERETT SALTONSTALL BUILDING, GOVERNMENT CENTER
100 CAMBRIDGE STREET, BOSTON 02202

OFFICE OF THE DIRECTOR
DIVISION OF WATER
POLLUTION CONTROL

March 6, 1974

Mr. Jack Conlon
Environmental Protection Agency
Region I
240 Highland Avenue
Needham Heights, Massachusetts 02194

Re: J.B.F. Scientific Corp.
Test Procedure

Dear Mr. Conlon:

We have reviewed the test plan submitted by J.B.F. Scientific Corp. on February 19, 1974 for evaluating their oil skimmers in Massachusetts waters.

We will concur with the test plan and have no particular additional requirements. Clean-up of previous tests by this firm has been satisfactory.

Very truly yours,

Thomas C. McMahon
Director

TCM/DLC/jf

cc: Mr. A. Bianchi, J.B.F. Scientific Corp., 2 Bay Avenue, Burlington, Massachusetts 01803

August 11, 1976

Ralph A. Bianchi
Project Director
JBF Scientific Corporation
2 Jewel Drive
Wilmington, Massachusetts 01857

Re: Boston Harbor
Oil Spill Tests

Dear Sir:

The Division of Water Pollution Control has reviewed the test plan submitted by JBF Scientific Corporation on July 23, 1976, titled:

Test Plans for Evaluating and Demonstrating
JBF Oil Skimmers in Boston Harbor.

JBF plans to demonstrate the effectiveness of four models of OIP skimmers by spilling and collecting oil in Boston Harbor waters. Biodegradable natural oils will initially be used for most tests, and fuel oil will be used to confirm the validity of those tests. The program will include clean-up in boomed off areas, tests involving new slicks, and tests of free slicks. Sorbents, piston films, gelling agents, and floating debris will be added to the slick during some tests to simulate natural conditions.

All tests will be in accordance with Section 610.3 of Title 18 of Federal regulations. JBF Scientific assumes all liabilities incurred as a result of the tests. The Division will be notified at least 24 hours in advance of all major tests.

The test plans are approved with the following conditions:

1. The results of the program will be sent to the Division.
2. A map of the proposed test locations at the shipyard should be sent to the Division.

Very truly yours,

Copy available to DDC does not
permit fully legible reproduction

Thomas C. McMahon
Director

TCM/JBF/ms

cc: Jack Conlan, EPA, 140 Highland Avenue, Needham Heights, Massachusetts 02194

APPENDIX C

TECHNICAL DATA

AMINE DTM AND DERIVATIVES

(Prepared by Hercules, Incorporated, Wilmington, Delaware)

Note: Some of the pages of this Appendix are independently numbered, or have no page numbers. Collectively, these pages comprise pages 61-69 of this overall Report.



TECHNICAL DATA

AMINE DTM AND DERIVATIVES

BULLETIN OR-132C
(Supersedes PC-132B)

AMINE D, AMINE D ACETATE 70%, AND AMINE D ACETATE 50S

AMINE DTM is a mixture of related primary amines derived from a modified rosin. It can be described chemically as a technical grade of dehydroabietylamine, the dominant amine comprising it. Amine D readily undergoes the usual chemical reactions of primary amines. For use in aqueous systems, it can be converted to the acetic acid salt, which is totally soluble in water. For the convenience of those who may not have facilities to convert to the acetate form, Hercules offers **AMINE D ACETATE 70%** and **AMINE D ACETATE 50S**, a 70 percent solids aqueous paste and a 50 percent solids aqueous-alcoholic solution of this salt, respectively.

This bulletin describes typical uses for Amine D and several of its derivatives, and presents detailed information on their physical and chemical properties. Toxicity and handling precautions are also included. Indicated applications include use as surface-active agents, corrosion inhibitors, additives for asphalt, industrial preservatives, chemical intermediates, and flotation reagents. A separate bulletin covers the Polyrad[®] series of ethylene oxide adducts of Amine D. This family of products is especially effective as inhibitors for acid-induced corrosion, particularly for hydrochloric acid.



HERCULES INCORPORATED • WILMINGTON, DELAWARE 19899

TYPICAL USES

Asphalt Additives

Amine D and its acetate salt are useful antistripping agents to improve or promote adhesion of asphalts to stone aggregates used in road construction or repair. They are more effective for improving binding of cutback asphalts to siliceous materials than to basic aggregates such as limestone. Generally, 0.5 to 1.25 percent of the amine or amine derivative is required, depending on type of asphalt and aggregate to be coated.

Chemical Intermediates

Amine D is a technical grade of the primary amine dehydroabietylamine, and, as such, is a very reactive chemical. It is used by Hercules and others for manufacture of acetate salts. Many other potentially useful derivatives (see section Chemical Reactivity under Chemical and Physical Properties of Amine D) can be made.

Corrosion Inhibitors

Reaction products of Amine D with ethylene oxide (Polyrad products) are highly effective corrosion inhibitors for hydrochloric acid used in chemical specialties (bowl cleaners), industrial cleaning, and oil well acidizing. These water-soluble inhibitors are especially useful in petroleum refinery streams for reducing corrosion of equipment by hydrogen sulfide, hydrogen chloride, carbon dioxide, and organic acids. In addition, these materials act as detergents in loosening and dispersing scale-forming materials present in refinery systems. Information in greater detail on Polyrad products is available in other Hercules literature.

Flotation Reagents

The acetate of Amine D is an excellent collector for silica and silicate minerals. It is used primarily in the beneficiation of nonmetallic ores such as feldspar, quartz, phosphate rock, and cement rock. It is useful also, alone or in conjunction with other reagents, for the beneficiation of iron oxide and other metallic ores. More detailed information on flotation applications of the acetate salt is available in another Hercules publication.

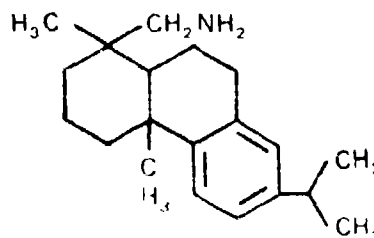
Preservatives

The pentachlorophenol salt of Amine D is a very effective ingredient of preservatives used in emulsion paints; wood-treating compounds; and cordage, felt, fabric, and paper that are not exposed to sunlight. The pentachlorophenate is neither manufactured nor sold by Hercules, but can be readily made by hot fusion of the above materials. A description of this derivative follows.

The pentachlorophenol salt of Amine D, which is sometimes referred to as technical dehydroabietylammmonium pentachlorophenoxide, is a dark amber, brittle, resinous solid. Softening point of a typical sample is 104°C; specific gravity at 20/20°C is 1.288. Vapor pressure of the pentachlorophenate is approximately one-tenth that of pentachlorophenol itself. The pentachlorophenate of Amine D is readily soluble in polar-type solvents such as pine oil, and in various aliphatic and aromatic hydrocarbons.

CHEMICAL AND PHYSICAL PROPERTIES OF AMINE D

Amine D is a mixture of high molecular weight primary amines derived from the resin acid constituents of a modified rosin. They are mainly stabilized abietyl-amines, the predominant one being dehydroabietylamine whose structural configuration is shown at the right. Typically, Amine D contains around 92 percent total amines of which about 3 percent are related secondary amines. It is a clear, yellow, viscous liquid having a faint ammoniacal odor. Other physical and chemical properties are shown below.



Typical Properties of Amine D

	<u>Amine D</u>
Color, Gardner	7
Specific gravity at 25/15.6°C	1.00
Refractive index at 20°C	1.545
Pounds per gallon at 25°C (kg/l)	8.3 (1.0)
Viscosity, poises at 25°C	87
Flash point, °F (°C)	378 (192)
Neutralization equivalent	316
Secondary amine content, %	3
Total amine content, %	92

Solubility - For all practical considerations, Amine D is insoluble in water. For example, solubility in water is less than 0.5 gram per 100 grams of water at 100°C. However, it is soluble in common organic solvents, including alcohols, ethers, hydrocarbons, and chlorinated solvents. For use in water or with aqueous systems, the amine can be reacted with acetic acid to form a water-soluble salt. Hercules offers the acetate salt of Amine D as a convenience to users who prefer to purchase rather than make the salt themselves.

Stability to Heat and Storage - Amine D is quite stable to heat below 100°C. Above this temperature, gradual decomposition occurs and increases as the heating time and temperature are increased. This is illustrated by the following data, on page 4, obtained on a typical sample of Amine D.

Time of Heating (days)	Temperature, °C	Weight Loss of Amine D During Heating, %
1	100	1.1
3	100	2.2
7	100	3.2
1	150	10.5
3	150	18.0
7	150	35.4
7.5 hours	203	14.9

The viscosity of Amine D decreases sharply with increase in temperature. When cold it is very viscous, but on warming it becomes sufficiently fluid to pump or otherwise transfer without difficulty.

Most metals are unaffected by Amine D under normal conditions of contact and storage. Laboratory tests showed no effect on black iron, stainless steel, Monel, copper, nickel, tin, zinc, or aluminum at room temperature. At 300°F (149°C), Amine D caused slight corrosion (approximately 2 mils per year) of black iron, Monel, nickel, tin, and zinc, but had no effect on stainless steel, aluminum, or copper.

Surface Activity Amine D facilitates the wetting of siliceous surfaces, as illustrated by the contact angle measurement data that follow.

Test Sample	Contact Angle Against Glass Immersed in Water (average value)
Mineral spirits alone	131°
Mineral spirits + 0.1% Amine D	114°
Mineral spirits + 1.0% Amine D	96°
Mineral spirits + 5.0% Amine D	77°

These tests were made by releasing drops of solution of Amine D in mineral spirits beneath glass plates submerged in water, in a horizontal position, and measuring the contact angle directly with a microscope. The smaller the angle, the greater the wetting.

Chemical Reactivity -- Amine D offers manufacturing chemists an unusual, high-purity, high molecular weight amine. As a chemical raw material or intermediate, it may be considered to be a technical grade of dehydroabietylamine, a condensed-ring-structure, partially aromatic primary amine whose structure is shown on page 3. It undergoes the many and varied reactions commonly associated with amines of this type. A few examples are its reaction with acids to produce amine salts, with alkyl halides to produce secondary and tertiary amines and amides, and with anhydrides to form imides. On the following two pages, in equation form, are other potential chemical reactions to which Amine D can be applied.

Particularly valuable derivatives of Amine D are the simple salts formed by reaction with carboxylic acids and acidic phenols. Examples are the salts of acetic acid and pentachlorophenol. The commercially available acetates of Amine D are discussed on page 7.

Possible Chemical Reactions of AMINE D (RNH₂)

Formula	Reaction of aniline with	According to These Equations
AMINO SALTS	a. Mineral Acids	$\text{RNH}_2 + \text{HCl} \rightarrow \text{RNH}_3^+ \text{Cl}^-$ $2 \text{RNH}_2 + \text{H}_2\text{SO}_4 \rightarrow (\text{RNH}_3^+)_2 \text{SO}_4^{2-}$
	b. Carboxylic Acids Naffion® Acids	$\text{RNH}_2 + \text{ClCH}_2\text{COOH} \rightarrow \text{RNH}_3^+ \text{CH}_2\text{COO}^-$ aniline • acetate $\text{RNH}_2 + p\text{-ClCH}_2\text{C}_6\text{H}_4\text{COOH} \rightarrow \text{RNH}_3^+ p\text{-ClCH}_2\text{C}_6\text{H}_4\text{COO}^-$ p-toluenesulfonate acid
	c. Organic Acids Phenols	$\text{RNH}_2 + \text{ClCH}_2\text{OH} \rightarrow \text{RNH}_3^+ \text{CH}_2\text{O}^-$ phenol • chlorophenol $\text{RNH}_2 + \text{penta-chlorophenol} \rightarrow \text{RNH}_3^+ \text{penta-chlorophenolate}$
N-SUBSTITUTED AMINES	a. Alkyl or Aryl Halides	$\text{RNH}_2 + \text{CH}_3\text{Cl} \rightarrow \text{RNHCH}_2\text{Cl}$ methyl • monomethyl salt ethyl $\text{RNH}_2 + \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \rightarrow \text{RNHCH}_2\text{C}_6\text{H}_5$ benzyl • monomethyl salt chloride
		$2 \text{RNH}_2 + \text{C}_2\text{H}_5\text{ClCH}_2\text{Cl} \rightarrow \text{RNHCH}_2\text{CH}_2\text{NRH}_2 + \text{HCl}$ ethylene • diamine salt chloride
		$\text{RNH}_2 + \text{CH}_3\text{CHCH}_3 \rightarrow \text{RNHCH}_2\text{CH}_3$ propene
	b. Alkylene Halides	$2 \text{RNH}_2 + \text{C}_2\text{H}_4\text{Cl}_2 \rightarrow \text{RNHCH}_2\text{CH}_2\text{NRH}_2 + 2 \text{HCl}$ ethylene • diamine salt chloride
		$\text{RNH}_2 + \text{CH}_2=\text{CH}_2 \rightarrow \text{RNHCH}_2\text{CH}_3$ propene
	c. Oxides	$\text{RNH}_2 + 2 \text{CH}_3\text{I} \rightarrow \text{RNHCH}_2\text{CH}_3 + \text{CHI}_3$ $\text{RNH}_2 + 2 \text{HCHO} + 2 \text{H}_2\text{O} \rightarrow \text{RNCH}_2\text{CH}_2\text{OH} + 2 \text{CO}_2 + 2 \text{H}_2\text{O}$
		$\text{RNH}_2 + \text{CH}_3\text{CH}_2\text{CH}_2\text{I} \rightarrow \text{RNHCH}_2\text{CH}_2\text{CH}_3$ propene
	a. Alkyl Halides	$\text{RNH}_2 + 2 \text{CH}_3\text{I} \rightarrow \text{RNHCH}_2\text{CH}_3 + \text{CHI}_3$
	b. Formaldehyde plus Formic Acid	$\text{RNH}_2 + 2 \text{HCHO} + 2 \text{H}_2\text{O} \rightarrow \text{RNCH}_2\text{CH}_2\text{OH} + 2 \text{CO}_2 + 2 \text{H}_2\text{O}$
	Alkyl Halides	$\text{RNH}_2 + \text{CH}_3\text{I} \rightarrow \text{RNCH}_2\text{CH}_3 + \text{HI}$
	Formaldehyde	$\text{RNH}_2 + \text{HCHO} \rightarrow \text{RNCH}_2\text{CH}_2\text{OH}$
N-ALKYL SUBSTITUTED AMINES	Formaldehyde	$\text{RNH}_2 + \text{HCHO} \rightarrow \text{RNCH}_2\text{CH}_2\text{OH}$ N-alkylmethylamine •
	Formaldehyde	$\text{RNH}_2 + 2 \text{HCHO} \rightarrow \text{RNCH}_2\text{CH}_2\text{CH}_2\text{OH}$ N,N-bis(hydroxyethyl)amine •
	Formaldehyde	$\text{RNH}_2 + 3 \text{HCHO} \rightarrow \text{RNCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ N,N-bis(hydroxypropyl)hydroxyethylamine •
	Formaldehyde	$\text{RNH}_2 + 4 \text{HCHO} \rightarrow \text{RNCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ N,N-bis(hydroxybutyl)hydroxyethylamine •
	Formaldehyde	$\text{RNH}_2 + 5 \text{HCHO} \rightarrow \text{RNCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ N,N-bis(hydroxypentyl)hydroxyethylamine •
N-ALKYL SUBSTITUTED AMINES	a. <i>p</i> -Toluenesulfonic Acids	$\text{RNH}_2 + p\text{-ClCH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H} \rightarrow \text{RNHCH}_2\text{C}_6\text{H}_4\text{SO}_3\text{Na} + \text{NaCl} + 2 \text{H}_2\text{O}$
	b. <i>m</i> -Toluenesulfonic Acids	$\text{RNH}_2 + m\text{-ClCH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H} \rightarrow \text{RNHCH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$ N-alkylmethyltoluenesulfonate
N-ALKYL SUBSTITUTED AMINES	Hydroxy-sulfonic Acids	$\text{RNH}_2 + \text{HOCH}_2\text{CH}_2\text{SO}_3\text{H} + 2 \text{NaOH} \rightarrow \text{RNHCH}_2\text{CH}_2\text{SO}_3\text{Na} + \text{NaOH} + 2 \text{H}_2\text{O}$ 2-(hydroxyethyl)sulfonic acid
	Acrylonitrile	$\text{RNH}_2 + \text{CH}_2=\text{CHCN} \rightarrow \text{RNHCH}_2\text{CH}_2\text{CN}$
DIARYLAMINES	Phenols	$\text{C}_6\text{H}_5\text{NH}_2 + \text{ClCH}_2\text{OH} \rightarrow \text{C}_6\text{H}_5\text{NHCH}_2\text{O}^-$

Possible Chemical Reactions of AMINE D (RNH₂)

Reaction	From Reaction of RNH ₂ With	According to These Equations
AMIDES AND IMIDES	a. Anhydrides of 1. Monocarboxylic Acids	$\text{RNH}_2 + \text{CH}_3\text{CO}_2\text{O} \rightarrow \text{CH}_3\text{CONHR} + \text{CH}_3\text{COOH}$ anhydride
	2. Dicarboxylic Acids	$\text{RNH}_2 + \text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H} \rightarrow \text{RNHCOCH}_2\text{CH}_2\text{COOH}$ succinic anhydride $\text{RNH}_2 + \text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H} \rightarrow \text{RNHCOCH}_2\text{CH}_2\text{CONHR} + \text{H}_2\text{O}$ maleic anhydride
	3. Acid Chlorides	$\text{RNH}_2 + \text{O}_2\text{CCH}_2\text{COCl} \rightarrow \text{O}_2\text{CCH}_2\text{CONHR} + \text{HCl}$ phthalic anhydride
	b. Acid Chlorides	$\text{RNH}_2 + \text{CH}_3\text{COCl} \rightarrow \text{CH}_3\text{CONHR} + \text{HCl}$ acetyl chloride
	c. Diethyl Oxalate	$\text{RNH}_2 + \text{CH}_3\text{SO}_2\text{Cl} \rightarrow \text{CH}_3\text{SO}_2\text{NHR} + \text{HCl}$ benzoyl chloride sulfonamide
N-SUBSTITUTED UREAS	a. Potassium Cyanate	$\text{RNH}_2 + \text{KOCN} + \text{HCl} \rightarrow \text{RNHCONH}_2 + \text{KCl}$
	b. Isocyanates	$\text{RNH}_2 + \text{R'NCO} \rightarrow \text{RNHCONHR'}$ (R' = alkyl or aryl)
	c. Urea	$\text{RNH}_2 + \text{H}_2\text{NCONH}_2 \rightarrow \text{RNHCONHCONH}_2 + \text{NH}_3$ $2\text{RNH}_2 + \text{H}_2\text{NCONH}_2 \rightarrow \text{RNHCONHCONHR} + 2\text{NH}_3$
N-SUBSTITUTED THIOUREAS	Carbon Disulfide	$2\text{RNH}_2 + \text{CS}_2 \rightarrow \text{RNHCONHSSRNH}_2$ N,N'-bis(phenylthio)thiourea
CHLORAMINE	Hypochlorous Acid	$\text{RNH}_2 + \text{HOCl} \rightarrow \text{RNHCl} + \text{H}_2\text{O}$
METAL COORDINATION COMPOUNDS OR AMINES	Metal Salts (cations: sodium, potassium, and ammonium; anions: Cu, Zn, Ag, N, Me, Ca, Hg, Co, Fe, Al, and Cr)	$2\text{RNH}_2 + \text{CH}_3\text{COOH} + \text{Ag}^+ \rightarrow \text{RNH}_2\text{CH}_2\text{COOAg} + \text{CH}_3\text{COOH}$ $2\text{RNH}_2 + \text{ZnCl}_2 \rightarrow \text{Zn}(\text{RNH}_2)_2$
PHOSPHONIUM COMPOUNDS	Phosphorus Chloride	$\text{RNH}_2 + \text{POCl}_3 \rightarrow \text{RNHPOCl}_2 + \text{HCl}$ $\text{RNHPOCl}_2 + \text{RNH}_2 \rightarrow \text{RNH}_2\text{P(OR)}_2 + \text{HCl}$ $\text{RNHPOCl}_2 + \text{RNH}_2 \rightarrow \text{RNH}_2\text{P(OR)}_2 + \text{HCl}$
SCHIFF'S BASES	a. Aldehydes	$\text{RNH}_2 + \text{C}_6\text{H}_5\text{CHO} \rightarrow \text{RNH}=\text{C}_6\text{H}_5 + \text{H}_2\text{O}$ benzaldehyde
	b. Ketones	$\text{RNH}_2 + \text{C}_6\text{H}_5\text{COCH}_3 \rightarrow \text{RNH}=\text{C}_6\text{H}_5 + \text{H}_2\text{O}$ acetophenone
IMIDES	Carbonyl Chloride	$\text{RNH}_2 + \text{COCl}_2 \rightarrow \text{RNHCOCl} + \text{HCl}$

CHEMICAL AND PHYSICAL PROPERTIES OF AMINE D ACETATE

The acetic acid salt of Amine D is commercially available from Hercules as Amine D Acetate. Two concentrations are offered: a 70 percent solids aqueous paste and a 50 percent solids aqueous-alcoholic solution. Properties of these products are shown below:

Properties of Amine D Acetate

	Amine D Acetate	
	70%	50S
Solids content, %	70	50
Water content, %	30	39
Isopropyl alcohol content, %	-	11
Specific gravity at 25/15.6°C	1.036	1.017
Pounds per gallon at 25°C (kg/l)	8.630 (1.04)	8.460 (1.02)
Viscosity at 25°C, poises	solid paste	1.070
Flash point, Tag. open cup, °F (°C)	-	140 (60)
Freezing point, °F (°C)	-	15 (-9)

Solubility - Amine D Acetate is quite soluble in water and lower molecular weight alcohols. Its solubility in most other organic solvents is not as great. In very hard waters, the presence of ions such as phosphate, chloride, and sulfate causes cloudy solutions. In waters of normal hardness, dilute solutions of the acetate (0.01 to 1 percent) may frequently be hazy, but higher strength solutions of from 1 to 50 percent are generally clear. Fifty percent concentrations are about the limit of solubility of the acetate in water at room temperature.

NOTE: The 50 percent solids commercial form of this acetate is readily diluted with water to lower concentrations. The most satisfactory dilution procedure for the 70 percent solids product, which is a heavy paste, is as follows: (1) add 1 part of water to 1 part of the paste and stir until mixture is uniform; (2) let stand 24 hours, after which the fluid paste can be readily diluted to any desired lower concentration.

Stability to Heat and Storage - The water- and alcohol-free acetate of Amine D is stable to heat below temperatures of around 90°C. Upon prolonged heating at higher temperatures, it is converted into the free amine and acetic acid, or to an N-substituted acetamide when the acetic acid formed cannot readily escape. For example, in a closed system, when a sample of the acetate of Amine D (100 percent solids) was heated 65 hours at 65°C, no change in composition occurred; when heated at 165°C for 1.5 hours, this salt was converted completely to an acetamide.

Stability to Air and Sunlight - A characteristic of high molecular weight primary amines and their salts is susceptibility to oxidation when thin films on various substrates are exposed to air in the presence of sunlight. Sunlight catalyzes the oxidation. In the absence of sunlight, oxidation is negligible. The acetate of Amine D, being a high molecular weight primary amine salt, also has this characteristic.

Surface Activity - The acetate of Amine D has definite surfactant properties. It shows marked wetting activity on siliceous surfaces. In aqueous solution, Amine D Acetate is adsorbed by cellulose fibers, threads, and fabrics, and, after drying, is not readily removed by subsequent washing. Also, the wetting time of cotton, as measured by the Draves method, is markedly decreased by the presence of small amounts of this salt in the water.

The following data illustrate these wetting properties, and show how surface tension and interfacial tension between water and organic liquids are decreased by the presence of this acetate:

Amine D Acetate (concentration in water, %)	0	0.01	0.10	0.15	0.175	0.20	0.50	1.00
Surface tension, dynes/cm at 25°C	72.1	55.4	37.7	-	-	33.4	33.4	-
Interfacial tension (isooctane-water), dynes/cm at 25°C	47.5	-	9.2	-	-	-	-	0.9
Wetting speed, Draves method (cotton), sec	-	-	180	50	18	9	-	-

TOXICITY AND HANDLING PRECAUTIONS

Like most amines and their salts, Amine D and the acetate, although of relatively low toxicity, should be handled with care. These products may cause skin irritation. Avoid prolonged or repeated contact with the skin.

Dermatological studies indicate that Amine D and certain of its derivatives are not skin sensitizers. At concentrations below 0.5 percent, they do not act as primary irritants even on prolonged exposure to the skin. However, concentrated solutions or the undiluted material on prolonged exposure do act as primary skin irritants, just as do many other amines and their salts.

If accidental contact is made with the skin, wipe off at once. In the case of Amine D, apply vinegar or a 5 percent solution of acetic acid and follow with thorough washing, using mild soap and water. The acetate salt form should be removed promptly by first washing with water followed by thorough washing with mild soap and water.

Should these products contact the eyes, immediately flush with plenty of water for at least 15 minutes, get medical attention. If spilled on clothing, remove and wash before reuse.

APPENDIX D

TEST OPERATIONS AT JBF CO. FACILITIES, 20 SEPTEMBER 1976

GELATION OF OIL SLICKS BY AMINE CARBAMATES AS AN ADJUNCT TO U.S. NAVY OIL SPILL
RECOVERY OPERATIONS. (Contract No. N00014-76-C-0349)

Test Operations at JBF Co. Facilities, 20 September 1976

I. Small quadrant test:

A. Sequence:

1. Apply 2 gal. Diesel Fuel to surface of pool.
2. Apply small quantities of Piston Oil Film to assist in containment of slick.
3. Spray 0.3 gal. (making for 15% vol./vol. concentration) of solution of Amine "D" (70% D, 15% ethyl alcohol, 15% benzyl alcohol) on surface of slick.
4. Apply powdered Dry Ice. Let stand for 5 minutes for gelation.
5. Recover gelled slick using sieve.
6. Apply Piston Oil Film to any residual ungelled oil.

B. Objectives:

1. Demonstrate spraying technique and subsequent application of CO_2 .
2. Demonstrate compatibility of Amine "D" system with Piston Oil Film.
3. Demonstrate sieving technique for harvesting of gelled slick.

II. Large quadrant test:

A. Sequence:

1. Apply 5 gal. of previously mixed No. 2 Fuel Oil/ Amine "D" soln.:
4.1 gal. No. 2. Fuel Oil (- 15% solution concentration, as above.
0.7 gal. Amine D soln. (-
2. Dust with powdered Dry Ice.
3. Harvest with DIP

B. Objectives:

1. Demonstrate harvesting technique and compatability with DIP.

C. Comments:

1. Pre-mixing necessary for this test inasmuch as sprayer will not reach all dimensions of large quadrant of pool.

III. Flame suppression test:

- A. Apply 1 mm film (75 ml.) of ungelled gasoline to surface of 10ft x 1" (deep) x 1½" (wide) trough filled with water.
- B. Ignite downwind end of trough and time spread of flame down trough.
- C. After fire ~~has~~ burned out, apply 75 ml of 85% gasoline - 15% Amine D solution to trough. Dust with powdered Dry Ice.
- D. Set fire to downwind end of trough; gelled film probably will not ignite or will burn very slowly down length of trough if ignition does occur.

IV. Fluorescence test: small quadrant. (Nighttime operation; optional)

A. Sequence:

1. Apply 2 gal. oil slick to small quadrant of pool.
2. Spray 0.3 gal. of Amine D solution to periphery of slick; this solution contains minute quantities of Rhodamine B dye.
3. Dust periphery of treated slick with Dry Ice powder.
4. After darkness, examine slick with UV ("Black") light to demonstrate nighttime visibility.

B. Objectives:

1. Demonstrate nighttime capability which could be derived from use of fluorescers.
2. Demonstrate capability of containment of oil slicks by use of peripheral treatments with amine gelants.

APPENDIX E

Correspondence from Scientific Officer, NRL



NAVAL RESEARCH LABORATORY

WASHINGTON, D.C. 20390

IN REPLY REFER TO:
8330-042:WDG;nep
01 March 1976

Dr. William W. Bannister
Department of Chemistry
University of Lowell
Lowell, Massachusetts 01854

Dear Dr. Bannister:

With regard to your progress report of 12 February 1976 (Contract No. N00014-76-C-0349), I find that your program is proceeding in a logical fashion. Your progress to date indicates that you will have a workable gelling agent in time for the planned field tests later in the year. I am particularly interested in your proposed studies of the effect of gelation on volatility. This will be a useful adjunct study relevant to the possible immobilization and hazard reduction in spills of flammable jet fuels and gasolines. In fact, I would suggest that more emphasis be given to volatility effects, if these studies indicate significant reductions in vaporation rate.

In the toxicity studies there may be an influence of the No. 2 fuel oil on the organisms tested. Perhaps fuel oil and the amine mixtures should be tested separately as well as in combination.

From a practical standpoint, your research should be geared to relatively thin oil layers. Small spills of distillate oils vary in thickness between 1 and 5 mm, while heavier petroleum fractions form films on water with thicknesses up to 1 cm. It might be interesting to study the effectiveness of gelation as a function of oil-film thickness.

Your proposed reporting schedule is satisfactory, and I wish you continued success in your future endeavors. Tentatively I plan a site visit to your laboratory during the week of April 19. There is a conference in Boston that week which I hope to attend. I will be in contact with you later to confirm this visit.

Best regards,

W. D. Garrett
W. D. GARRETT, Head
Interface Chemistry Section
Ocean Sciences Division

cc: NAVFAC 0320 (S. M. Hurley)



NAVAL RESEARCH LABORATORY

WASHINGTON, D.C. 20375

IN REPLY REFER TO:

8330-171:WDG:mc

27 July 1976

William W. Bannister
Department of Chemistry
University of Lowell
Lowell, MA 01854

Dear Dr. Bannister:

Your progress report No. 4 of 8 July 1976 on the project "Gelation of Oil Slicks by Amine Carbamates as an Adjunct to U.S. Navy Oil Spill Recovery Operations" has been reviewed. The work is on target and in accordance with the contract assignments. I especially appreciate your willingness to follow the guidelines outlined in my letter of 1 March, which suggested minor modifications in the research direction.

The additional research performed by your group on the reduction of flammability hazards in volatile fuels through gelation may prove to be of future value to the transport and handling of petroleum products. Although flammability reduction is not a part of the contract work statement, I hope that you have the opportunity to determine flame propagation rates of gelled vs. ungelled fuels. Such studies could be performed in open trench tests of the kind we discussed during your 22 July visit to NRL.

In recent telecons with you and Mr. Bianchi of JBF Scientific Corporation, it was determined that field evaluations of the developed gelation system will be performed in September (tentative date, week of 20 Sept.) in the JBF test tank. It is anticipated that these studies will be designed to achieve the following goals:

- (1) Determination of the feasibility of in situ oil spill gelation using the developed amine carbamate approach under field conditions.
- (2) Evaluation of the effectiveness of devices for applying gelation agents.
- (3) Studies of the ability of oil-spill removal systems to harvest the gelled petroleum oil.
- (4) Determination of the possibility of premixing the amine and CO₂ prior to their contact with the floating oil and the properties of the gel produced by such a procedure.



8330-171:WDG:mc

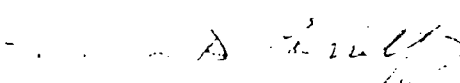
27 July 1976

Page 2

- (5) Oil-collecting agents (Piston Film) will be used to confine some of the test spills to determine the advantage of preventing spreading of the spill prior to gelation.

With regard to the latter study, I have supplied two 1-pint cans of the Navy piston film (Federal Stock No. 6810-172-9110) to JBF for use in the September test-tank evaluations. Thank you for your invitation to observe and participate in the field studies. I will endeavor to contribute to their success.

Very truly yours,


William D. Garrett, Head
Interface Chemistry Section
Ocean Sciences Division

cc: S. M. Hurley, NFAC 032 B
R. A. Bianchi, JBF Scientific Corp.